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Sediment Contact Tests - Reference conditions, control sediments, toxicity thresholds. Symposium on 13/14 November 2008 in Koblenz

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Sediment Contact Tests

Reference conditions, control sediments, toxicity thresholds

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Vorwort

Vor dem Hintergrund der Umsetzung der Europäischen Wasserrahmenrichtlinie besteht derzeit ein großer Forschungs- und Entwicklungsbedarf hinsichtlich der Anwendung von Kontakttests zum Nachweis des ökotoxikologischen Schädigungspotenzials von Sedimenten. Während die bisherigen aquatischen Biotestverfahren die tatsächliche Bioverfügbarkeit von Schadstoffen nur unzureichend berücksichtigen, besitzen Sedimentkontakttests die höhere Relevanz für das Ökosystem, da sie realistische Expositonsszenarien simulieren. Das SeKT-Verbundprojekt wurde mit dem Ziel initiiert, kürzlich entwickelte oder standardisierte Sedimentkontakttests zu vergleichen und die praktische Anwendbarkeit von Sedimentkontakttests für ein möglichst weites Spektrum unterschiedlicher Sedimente zu überprüfen. Dabei wurde darauf geachtet, dass in der Palette an Toxizitätstests Repräsentanten verschiedener trophischer Ebenen als Testorganismen eingesetzt wurden, die außerdem eine große Bandbreite an Expositionspfaden im Sediment berücksichtigen (Bakterien, Pilze, Nematoden, Oligochaeten, Fische, höhere Pflanzen).

Im Symposium wurden, neben der abschließenden Darstellung der Ergebnisse des Verbundprojekts, vor allem die Anwendungsmöglichkeiten von Sedimentkontakttests mit Experten vieler verschiedener Disziplinen diskutiert. Dem SeKT-Konsortium war es sehr wichtig, internationale Experten aus Wissenschaft, Behörden und Industrie als Redner zu gewinnen, um das Thema aus verschiedenen Blickwinkeln betrachten zu können. Das Symposium wurde deshalb in vier verschiedene Blocks eingeteilt: Wissenschaft, Standardisierung, Sedimentmanagement und Monitoring. Auf diese Weise ist es gelungen eine Veranstaltung zu gestalten, die sich sowohl an Wissenschaftlerinnen und Wissenschaftler der angewandten Umweltwissenschaften als auch an Fachleute in den Umweltverwaltungen des Bundes und der Länder, die mit der ökotoxikologischen Bewertung stofflicher Wirkungen in der Umwelt befasst sind, richtete.

Wir möchten uns herzlich bei allen SeKT-Projektpartnern für die intensive Zusammenarbeit bedanken sowie bei den Vortragenden und Teilnehmern des Symposiums für die interessanten Veranstaltungsbeiträge. Besonderer Dank gilt unserem wissenschaftlichem Beirat Ulrich Förstner, Hans-Jürgen Pluta, Axel Netzband, Piet den Besten, die nicht nur als Vortragende, sondern auch während des Projekts einen wertvollen Beitrag zum Gelingen des Projekts beigetragen haben. Insbesondere danken wir auch Frau Yvonne Strunck, BfG, für die hervorragende Organisation. Ebenso gilt unser Dank dem Bundesministerium für Forschung und Bildung für die Förderung des Verbundprojekts (BMBF FKZ 02WU598-02WU604).

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Preface

Against the background of the implementation of the European Water Framework Directive (WFD) there is currently a high demand for research and development regarding the application of contact tests to detect potentials in sediments to cause ecotoxicological damage. While conventional aquatic biotest methods do not sufficiently account for the actual bioavailability of contaminants, sediment contact tests are more relevant for the ecosystem since they simulate realistic exposure scenarios. The joint research project SeKT – the acronym stands for the German word '**Se**diment**K**ontakt**T**ests' (= sediment contact tests) – was initiated with the aim to compare recently developed or standardized sediment contact tests in terms of their variability and practical applicability in sediments with a wide range of properties. The test battery was carefully selected to include test organisms that represent different trophic levels and cover a broad variety of exposure pathways in the sediment (bacteria, fungi, nematodes, oligochaetes, fish, and higher plants).

Following a final presentation of the results of the project, the symposium provided a platform for discussion on the applications of sediment contact tests among experts of many disciplines. The organizers had placed great emphasis on the acqusition of international experts from sciences, administration, and industries as speakers to examine the topic under a variety of aspects. The symposium was structured in four blocks: research, standardization, sediment management, and monitoring, so that the meeting addressed representatives of applied environmental sciences as well as specialists from environmental authorities of the Federal government and Federal states who are engaged in ecotoxicological assessments of chemical impacts on the aquatic environment.

On this occasion we want to thank all partners in the SeKT Project for the close cooperation and all lecturers and listeners at the symposium for their contributions. Special thank is due to our scientific advisory council with Ulrich Förstner, Hans-Jürgen Pluta, Axel Netzband, Piet den Besten, who contributed not only as speakers but had given valuable inputs throughout the project. What must not be forgotten is the thank to Frau Yvonne Strunck, BfG, for the excellent preparation and organization of our meeting. Finally we thank the German Federal Ministry of Research and Education for the funding of this joint research project (*BMBF FKZ 02WU598-02WU604*).

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Sediment contact tests as a tool for the assessment of sediment quality in German rivers (SeKT-project)

Ute Feiler and Peter Heininger

Zusammenfassung

Das SeKT-Projekt zielte darauf ab, die Anwendbarkeit einer Sedimentkontakttestbatterie durch die Untersuchung einer Vielzahl verschiedener Sedimente zu überprüfen und ihre Zuverlässigkeit zu verbessern. Durch die Bestimmung der MDDs (minimal detectable difference) konnten einerseits Informationen zur testinternen Variabilität jedes beteiligten Sedimentkontakttests erlangt werden. Andererseits wurde die matrixbedingte Variabilität der Testergebnisse durch die Errechnung der MTIs (maximal tolerable inhibition) ermittelt. Durch die Bestimmung dieser beiden Variationskoeffizienten wurde die Verlässlichkeit der Testergebnisse verbessert. Sie ermöglichten die Definition von testspezifischen Toxizitätsschwellenwerten, die wiederum eine bessere Interpretation der Ergebnisse zulassen.

Bei der Untersuchung von kontaminierten, natürlichen Sedimenten mit den Sedimentkontakttests aus dem SeKT-Projekt, konnten unter Verwendung der abgesicherten statistischen Parameter, signifikante Wachstumshemmungen der jeweiligen Testorganismen beobachtet werden. Aus der Zusammenschau der Ergebnisse der Sedimentuntersuchungen im Rahmen des SeKT-Projekts wurde eine Sedimentklassifizierung hinsichtlich der Sedimenttoxizität, basierend auf den vielfachen toxischen Effekten vorgeschlagen.

Die Sedimentkontakttestbatterie eignete sich also für die Bewertung von Gewässersedimenten und sollte folglich bei zukünftigen Sedimentmonitoringprogrammen eingesetzt werden. Die Ergebnisse aus dem SeKT-Projekt können als Datengrundlage für eine verbesserte Interpretation und Auswertung ökotoxikologischer Sedimentdaten verwendet werden.

1 Introduction

For decades, the contamination of river and lake sediments has increased rapidly. Sediments have been recognized both as a major sink and as a potential source of persistent toxic substances released into the aquatic environment (BRILS 2002, FÖRSTNER 2004, SedNet 2004). Therefore, sediments – being the habitat of an abundant biocoenosis and the place for a multitude of biochemical transformations – play a key role in the assessment of the ecological status of waters. Sediment studies are very suitable for highlighting the extent and the trend of water pollution. In Germany, up to 4 million m³ of sediment are dredged per year in inland waterways. Among others, toxicity criteria are used to decide on the acceptable relocation or disposal pathway of dredged material that may differ significantly in their costs. Therefore, thorough sediment characterisation is essential. At present, the concept of the triad approach, i. e. a combination of chemical analyses, ecotoxicological investigations (standardized bioassays), and investigations of the benthic community structure (CHAPMAN 2000), is a widely accepted approach to assessing the environmental hazard of sediment-bound contaminants. Despite the broad consensus in the scientific world that whole-sediment exposure protocols are indispensable for a realistic scenario of simulating *in situ* exposure conditions, in many cases exclusively *aquatic* bioassays are demanded by valid environmental regulations and guidelines. For example, a standardised bioassay battery using aquatic organisms of the three trophic levels – producers (algae), consumers (crustacea), and decomposers (bacteria) – is part of the guideline for the assessment of dredged material in German Federal waterways (HABAB WSV 2000).

Recently developed solid-phase assays comprise contact assays with bacteria (DIN 38412-48, RÖNNPAGEL et al. 1995, HEISE & AHLF 2005, NEUMANN-HENSEL & MELBYE 2006), nematoda (TRAUNSPURGER et al. 1997, KAMMENGA et al. 1996), oligochaetes (EGELER et al. 2005), chironomides (OECD 218), vertebrates (HOLLERT et al. 2003, KEITER et al. 2006), macrophytes (FEILER & KREBS 1999, FEILER et al. 2004, 2006 a, b), and yeast (WEBER et al. 2006). The complexity of the sediment matrix (particles and water) places high requirements on the biological test methods. The bioassays must be able to distinguish between anthropogenic impacts (contamination) and the influences of natural factors (e. g. the grain-size spectrum), thus making risk assessments possible. The SeKT joint research project (SeKT = **Se**diment-**K**ontakt-**T**est) was initiated with the aim to compare recently developed sediment contact assays by addressing reference conditions, control sediments, and toxicity thresholds for their application in freshwater sediment toxicity assessment (FEILER et al. 2005).

2 Project plan of the SeKT joint research project

The studies of SeKT aimed to describe the applicability of sediment contact tests and to improve their reliability. A wide range of sediments, in terms of their structure and main components, was tested to determine the variability of the results of a defined test battery. The crucial steps of the project plan were (i) the application of the sediment contact tests to different unpolluted natural sediments in order to identify the influences of natural sediment properties on the test systems, (ii) the definition of reference conditions, including the standardization of negative controls, (iii) the determination of toxicity thresholds for the individual sediment contact tests. Furthermore, (iv), the test systems should be validated with contaminated natural sediments and by means of dose-effect relations with sediment samples that were spiked with selected contaminants. The results obtained within the project should serve as data base for improved interpretation and evaluation of ecotoxicological sediment analyses.

3 The SeKT consortium

The SeKT consortium is shown in Figure 1. It consists of seven partners representing (i) the German Federal Institute of Hydrology, (ii) two Universities and (iii) four small to medium-sized specialised enterprises (SMEs).

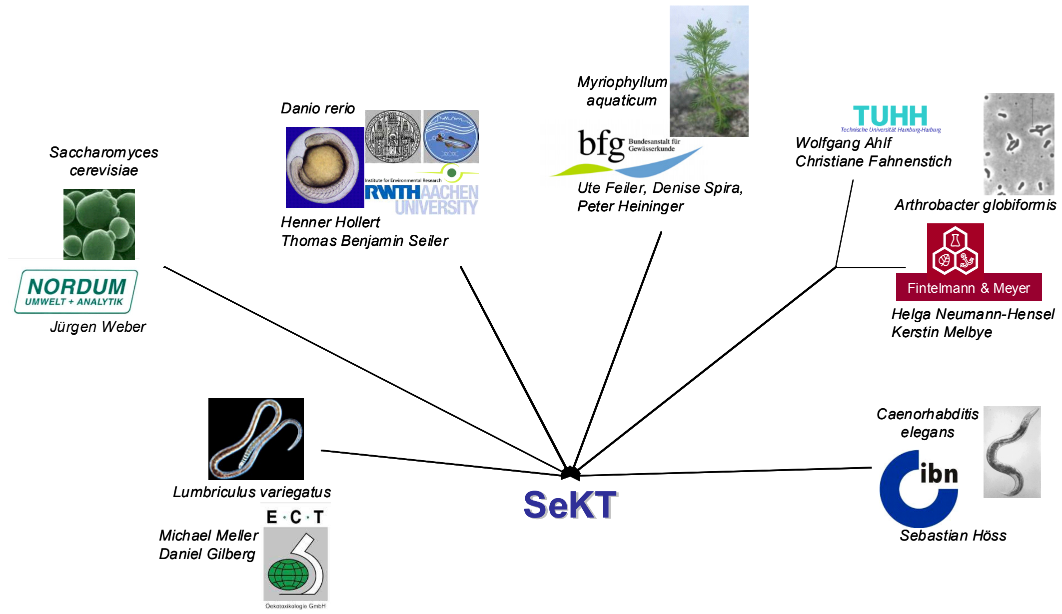

Figure 1: The SeKT consortium

4 The SeKT test battery

The SeKT test battery is listed in Table 1. Selection criteria for including a certain sediment contact test were:

> The test systems are published or standardized.

> They have a good record of applications in a wide range of problems.

> The test organisms are representing different organisation levels and represent the three trophic levels (producers, consumers, decomposers).

> Several uptake pathways and toxicity endpoints are considered.

Table 1
The SeKT test battery

Test	Published / standardised in	Test organism	Organisation level	Trophic level	Pathway	Endpoint
Yeast test	Weber et al. (2006)	*Saccharomyces cerevisiae*	Yeast	Decomposer	Pore water, particle contact	Fermentation
Bacteria test	ISO/WD 10871, DIN 38412-48	*Arthrobacter globiformis*	Bacteria	Decomposer	Pore water, particle contact	Metabolism
Oligochaete test	Egeler et al. (2005)	*Lumbriculus variegatus*	Invertebrate	Consumer	Pore water, particle contact, particle ingestion	Growth, reproduction, bioaccumulation
Nematode test	ISO/CD 10872	*Caenorhabditis elegans*	Invertebrate	Consumer	Pore water, particle contact, particle ingestion	Growth, reproduction
Fish-egg test	Hollert et al. (2003)	*Danio rerio*	Vertebrate	Consumer	Pore water particle contact	Mortality
Myriophyllum test	Feiler et al. (2004)	*Myriophyllum aquaticum*	Plant	Producer	Pore water, particle contact	Growth

5 Definition of reference conditions (control sediments, toxicity thresholds)

The first working-package of the SeKT-project aimed to define a control sediment which was applicable as negative control for all SeKT test systems. For this purpose, eleven non- or minor polluted natural sediments and five artificial sediments were tested. The natural sediments were selected to cover (i) various river basins, (ii) different types of suface waters, (iii) a scale of anthropogenic impacts beyond pollution, (iv) a wide grain-size spectrum, and (v) a wide spectrum of the content of organic carbon (TOC). In addition, several artificial sediments were tested, which had been proven earlier as control media in standard tests (e. g. OECD-218 Chironomid test). As a result, two natural sediments from both a river and a lake and one artificial sediment were defined as control sediments for the entire SeKT test battery. The influence of basic sediment properties on the individual test systems is widely discussed with respect to the validity of the test results. Therefore, the variability of the results from the SeKT test systems was studied in this work-package. First, the test-inherent uncertainty – i. e. the variability of test parameters between several replicates of one sediment with low contamination – was calculated as mean MDD (MDD, minimal detectable difference). Second, the matrix-related uncertainty – i. e. the variability of the test parameters between different, non- or minor polluted sediments – was calculated as MTI (MTI, maximal tolerable inhibition). From these values, toxicity thresholds were determined for most of the SeKT test systems.

6 Sensitivity of the sediment contact tests

The two control sediments (river sediment, artificial sediment) that had been defined in the first part of the SeKT project were used for spiking experiments in a second working package. Both sediments were spiked by two different mixtures of pollutants, including heavy metals and organic substances, respectively. Combining the results of the different test systems and applications, a wide range of EC50-values was calculated, indicating different exposure pathways and sensitivities for the various test organisms. Different toxicity of metals and organic substances in artificial sediments compared to natural samples was observed for all test systems. Differences in the bioavailability of the toxicants due to their specific binding properties might be the reason. Generally, the results indicate that the proposed sediment contact tests complement each other. They represent the potential exposure pathways and the trophic levels of benthic habitats. The contact tests with plants, nematodes, oligochaetes, and fish-eggs proved to be the most sensitive.

7 Application of the SeKT test battery on anthropogenically polluted sediments

In the third working package of the project, the SeKT-battery was applied to polluted sediments from diverse German rivers. As control sediments the artificial sediment and the two natural sediments were used in all test systems, and the toxicity thresholds that had been found in the first working package were applied. Ten polluted natural sediments were selected according to the above-mentioned criteria, however, now emphasizing on a high load of pollution, and tested with the SeKT-battery. A wide variety of toxic effects was observed. The inhibition values ranged from "no effect" to almost 100%, depending on the test system and the sediment studied. Thus, within the range of tested sediments, a classification in terms of toxicity was possible, based on the multiple toxic effects detected by the test systems.

Summary

The studies within the SeKT project had the objective to test the applicability of a sediment contact tests battery with a possibly wide range of different sediments. By determining the MDDs, information on the test-internal variability of each SeKT test result was obtained. The variability due to natural sediment properties is reflected by the MTIs. Defining both the MDDs and the MTIs, the reliability of the SeKT test systems could be improved. The determination of toxicity thresholds allows a better interpretation of the test results. Using the ascertained statistic parameters, significant growth inhibition could be distinguished by the investigation of polluted natural sediments with the SeKT test battery. The sediment contact test battery proved to be suitable for the assessment of river sediments and should be used in future sediment monitoring. The results obtained within the project can also be used as a data base for an improved interpretation and evaluation of ecotoxicological sediment data.

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Evaluation of toxicity and bioavailability of chemicals in sediments

Jussi V. K. Kukkonen

Zusammenfassung

Sedimente wirken als Senken und Quelle für verschiedene Schadstofftypen, weshalb sie bei Risikobewertungen hinsichtlich der Ökologie und der menschlichen Gesundheit angemessen berücksichtigt werden sollten. Angesichts der Bedeutung der Bioakkumulation durch Benthosorganismen werden dafür zuverlässige, kostengünstige Methoden zur Bestimmung der Rate und der Menge der akkumulierten Schadstoffe benötigt. Standardisierte Testmethoden zur Bewertung der Bioakkumulation sedimentbürtiger Schadstoffe sind erforderlich, um Kriterien der Sedimentqualität zu definieren (DI TORO et al. 1991) und damit die potenziellen Auswirkungen von Baggergutablagerungen abzuschätzen.

Der Beitrag diskutiert verschiedene Aspekte der Bioakkumulation von der Verfügbarkeit von Schadstoffen über den im Organismus verbleibenden Anteil bis zur Bestimmung von Wirkungen.

Evaluation of toxicity and bioavailability of chemicals in sediments

Sediments act as a sink and a source for different types of contaminants. Thus, sediment exposure evaluations should be an important component for both ecological and human health risk assessments. Credible, cost-effective methods are required to determine the rate and extent of bioaccumulation given the potential importance of bioaccumulation by benthic organisms. Standardized test methods to assess the bioavailability of sediment-associated contaminants are required to assist in the development of well defined sediment quality criteria (DI TORO et al. 1991) and to assess the potential impacts of disposal of dredge materials.

The extent to which sediment-associated contaminants are biologically available and bioaccumulated is important in order to assess their direct effects on sediment-dwelling organisms and assess their transport to higher trophic levels. More well designed studies are required to determine the potential for bioaccumulation that can be interpreted and modelled for predicting the impact of accumulated chemicals. This is a demanding work because, bioavailability of any given contaminant is not a constant factor but rather an organism and system dependent parameter. The ecology and behaviour of organisms in the given environment is one important factor determining potential bioaccumulation of contaminants. Accurate prediction and evaluation of xenobiotic contaminant exposure and accumulation from sediments remains difficult because of the complex interactions between the contaminant, the sediment, and the organism. These interactions depend for example on:

1) chemical characteristics and concentration of the contaminant;
2) physical and chemical characteristics of sediments;
3) the presence of complex mixtures that can confound the contaminant interactions with both the sediment constituents and the biota;
4) organism behaviour and physiology influenced by such environmental factors as temperature, nutrient availability, and habitat that can modify the exposure both between species and temporally within a species; and
5) the length of sediment/contaminant contact time that can change bioavailability (LANDRUM et al. 1996).

Interaction of hydrophobic contaminants with natural dissolved organic material or particulate material plays a major role in contaminant distribution and bioavailability in the environment. For non-polar organic compounds the binding affinity is generally directly related to the hydrophobicity of the contaminant and the organic content of a sorbent such as particles. However, partitioning and bioaccumulation studies indicate that contaminant sorption and bioavailability may also be affected by different forms of organic carbon. Partitioning between water and particles has been described in multi-kinetic processes that appear as two differentially bioavailable pools: one in a reversible pool and another in a resistant pool. The fraction of contaminant that resides in each of these pools changes, depending upon the sorption duration. During this equilibration phase, contaminant bioavailability can also be expected to change with time. It has been demonstrated that the fraction of the sediment-associated contaminant that exists in a rapidly desorbable pool is correlated with the bioavailability of the contaminant across a set of contaminants in a single sediment (KRAAIJ et al. 2001). However, the relationship is not so clear when several sediments are included (KUKKONEN et al. 2003, 2004, 2005). Thus, it appears that the bioavailability across sediments may partly be explained by the ability of contaminants to desorb from sediments.

Bioavailability of contaminants in the environment is measured as bioaccumulated body burden in organisms. This shows the net exposure of the organism to a contaminant from various source compartments over time. Further, it represents the balance between the flux into the organism and the loss through protective processes such as biotransformation and elimination. The importance of bioaccumulation is its direct link between the external contaminant concentrations in the sources and the potential effect of contaminants at various levels of biological structure and function. Bioaccumulated contaminants that attain sufficient concentration at a receptor site of a living organism for sufficient duration are responsible for exerting the pharmacological and/or toxicological effect of the compound on the same organism.

Our understanding and interpretation of the impact of environmental contaminants can be improved by examining the relationship between body residues and biological responses in laboratory exposures and in the field. The concept using the body residue as a dose metric was first presented by MCCARTY (1986) and its potential for use in risk assessment was further developed by MCCARTY & MACKAY (1993). In most cases, the data in the literature use mortality as the endpoint for consideration (for example KUKKONEN 2002). However, a few studies have examined development time, growth, and reproduction to assess sublethal chronic responses (FISHER et al. 1999, HWANG et al. 2001). The use of chronic measures will better reflect the conditions expected to occur in the environment. Since organisms, particularly benthic organisms, spend large portions of their life cycle exposed to contaminated sediments, the body residue provides a better measure of real exposure than the sediment concentration because interpreting bioavailability remains problematic.

The sediment contact tests are recommended because they can provide a direct measure of benthic effects at contaminated sites. The other advantages include that the testing requires a limited number of special equipments and most of the methods are relatively inexpensive and rapid (exposures up to 28 days). The widely accepted procedures already exist to conduct these tests (OECD, ASTM standards) and the exposures with spiked chemicals provide data on cause-effect relationships to the chemicals of concern. Further, these tests can be easily applied to field samples when site specific questions are involved. Unfortunately the sediment contact test may have some limitations too. Sediment collection, handling and storage may alter the bioavailability and toxicity of chemicals present in contaminated sediments. The spiked sediments may not be representative of field contaminated sediments because of different contact times and handling. The sediment characteristics, besides the chemicals, may affect the response of test organisms and overall the laboratory tests have their limitations in predicting the long term ecological effects.

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Ecological risk assessments on aquatic-terrestrial gradients in a freshwater tidal area

Jaap Postma, Rineke Keijzers, Jack Faber and Piet den Besten

Zusammenfassung

Ökologische Risikobewertungen werden im Allgemeinen getrennt für terrestrische und aquatische Systeme vorgenommen, obwohl diese Systeme oftmals benachbart sind. Das Ziel dieser Studie war ein Vergleich der ökologischen Risiken entlang eines Gradienten von den aquatischen zu den terrestrischen Bedingungen. Die Bewertung unfasste chemische Analysen (einschließlich der bioverfügbaren Anteile) sowie Bioteste und Experimente zur Bioakkumulation sowohl mit aquatischen als auch terrestrischen Organismen. Die Ergebnisse zeigen, dass Sedimente und Böden aus benachbarten aquatischen und terrestrischen Systemen unterschiedliche Bewertungen hinsichtlich der ökologischen Risiken ergeben können. Für Oligochaeten scheint die Verfügbarkeit von Metallen im aquatischen Milieu im Vergleich zur terrestrischen Umgebung begrenzt zu sein, während bei organischen Schadstoffen das Gegenteil beobachtet wurde. Der Beitrag zeigt in der Zusammenschau den Einsatz unterschiedlicher Bewertungsverfahren zur vergleichenden Beurteilung ökologischer Risiken in aquatischen und terrestrischen Lebensräumen.

Abstract

Ecological risk assessments are generally performed for either terrestrial or aquatic systems, while these systems sometimes exist in close proximity. The objective of this study was to compare environmental risks along gradients from aquatic to terrestrial conditions. The assessment involved chemical analysis (including bioavailable fractions), as well as bioassays and bioaccumulation experiments using aquatic and terrestrial organisms. The results demonstrate that sediments and soils from neighbouring aquatic and terrestrial systems may render different assessments in terms of environmental risks. Metal availability for oligochaetes appeared to be limited in the aquatic environment as compared to the terrestrial environment, while the reverse was observed for organic contaminants. The presentation aimed to illustrate the use of various assessment techniques within a framework to compare ecological risks in aquatic and terrestrial environments.

1 Introduction

In tidal areas and river flood plains the sources of contamination in the semi-aquatic and terrestrial soils are similar to those in adjacent aquatic sediments. Decision-making on possible remedial actions is improved by a good understanding of ecological risks associated with the contamination. Such assessments should cover both aquatic as well as terrestrial aspects and should make a direct comparison between these two parts of the ecosystem as much as possible. Only on the basis of such integrated assessment remedial actions can be directed towards those aspects from which the ecosystem most strongly benefits.

To gain insight in the comparability of environmental risks in closely linked aquatic and terrestrial systems, a study was undertaken in a freshwater tidal area, the Sliedrechtse Biesbosch in the Rhine-Meuse Delta in the Netherlands. Because of seasonal high river discharges, the area is flooded once or twice each year, having caused widespread contamination of the terrestrial as well as the aquatic environment. Previous studies indicated serious environmental risks in the aquatic environment (DEN BESTEN et al. 1995; PEETERS et al. 2001), but little or no information is available concerning the terrestrial environment. This study aimed at the development of an approach, suitable for areas where both aquatic and terrestrial systems exist in close proximity.

2 Materials and methods

2.1 Test materials

Sediments and soils were sampled along two sites comprising gradients of aquatic to terrestrial locations, 1) shallow water, 2) shallow water with reeds, 3) an intertidal mud flat, 4) reed vegetation, and 5) a marsh forest. These five locations were each sampled at two transects, "Sneepkil" (S) and "Gat van de Hengst" (G), used as replicates. Sample locations were carefully selected, trying to keep the total concentrations of the contaminants constant along the gradient as well as between the two sites.

2.2 Analyses

Physico-chemical:
All samples were analysed on organic carbon content, particle size distributions, metals (total and 0.01 M $CaCl_2$-extractable concentrations of Cd, Cu, Pb, Ni, Zn, Cr, Hg and As) and several organic contaminants (total and Tenax extractable concentrations of PAHs, PCBs, pentachlorobenzene, hexachlorobenzene, p,p'-DDD and p,p'-DDE).

Bioassays and bioaccumulation tests:
Samples were tested using the following bioassays: Microtox (ISO 11348-3), *Daphnia magna* (OECD 202), *Chironomus riparius* (VAN DE GUCHTE et al. 1993), *Limnodrilus sp.* (only bioaccumulation), *Folsomia candida* (ISO 11267), *Lumbricus rubellus* (ISO 11268-2). Selected toxicity tests were performed according to the origin of the sample, aquatic tests on sediments, and terrestrial tests on soils. Samples from the intertidal mud flats were tested with all organisms to facilitate the comparison of ecological risks. Furthermore, the Microtox and a bioaccumulation assay were performed on all samples.

Table 1
Concentrations of metals and organic contaminants (mg/kg dry wt) in sediments and soils from aquatic (1) – terrestrial (5) gradients at Sneepkil (S) and Gat van de Hengst (G).

Sampling location	Shallow water		Shallow water with reed		Intertidal mud flat		Reed vegetation		Marsh forest	
	S1	G1	S2	G2	S3	G3	S4	G4	S5	G5
Carbon content (‰)	45.0	39.6	46.1	52.5	49.3	47.4	81.3	69.2	119.8	84.3
Metals (mg/kg dry wt)										
As	48	58	47	47	42	39	49	83	48	106
Cd	5.4	6.3	5.5	5.1	4.7	4.0	5.4	10.5	5.9	12.3
Cr	134	130	115	130	120	109	136	258	147	318
Cu	90	75	77	87	82	73	96	159	98	177
Pb	159	146	138	159	148	137	168	301	185	400
Ni	44	33	36	47	42	41	49	54	52	77
Zn	615	633	597	612	556	493	644	881	671	1355
Hg	2.1	1.6	2.7	1.9	1.9	1.7	2.1	2.7	2.1	6.2
Organic contaminants (mg/kg dry wt)										
Σ 13 PAHs	6.2	9.9	6.4	6.6	6.8	5.5	5.5	6.3	6.4	6.1
Σ 7 PCBs	0.2	0.3	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.2
p.p'-DDE	0.003	0.004	0.002	0.002	0.002	0.003	0.003	0.002	0.005	0.004
p.p'-DDD	0.004	0.006	0.004	0.005	0.003	0.004	0.004	0.004	0.004	0.003

3 Results

3.1 Physico-chemical analysis

Metals:
As desired, total metal concentrations were fairly constant along the aquatic-terrestrial gradients, although especially in two terrestrial samples (G4 and G5) higher concentrations were found (factor 2). The possible influence of the total metal concentration on the available fraction will consequently be small. In most cases $CaCl_2$-extractable fractions obtained from the original field collected sediment were lower than fractions in the dried samples. Lead and chromium were exceptions, showing no significant relationships between the two extraction procedures, whilst these relations were only weak for arsenic. In addition, the $CaCl_2$-extractable fractions of these three metals did not vary along the gradients from shallow water to marsh forest (data not shown). The $CaCl_2$-extractable fractions of cadmium, zinc, copper, and nickel on the other hand clearly increased along the gradients. Furthermore, the dried samples yielded higher extractable fractions compared to the field collected samples (illustrated in figure 1 for the mud flat samples).

Organic contaminants:
No significant differences were found in the total concentrations of PAHs, PCBs, DDE and DDD along the gradients from aquatic to terrestrial locations. Significant differences were however found after correction for the organic carbon content, since the terrestrial locations were characterized by significant higher organic carbon contents (OC normalized data not shown, but organic carbon contents are presented in table 1). In contrast to the total concentrations, statistically significant differences were found in the bioavailable fraction as measured by the Tenax fraction. The Tenax extractable fraction of PAHs, PCBs, DDE and DDD decreased at terrestrial locations as carbon contents increased (Figure 1).

3.2 Bioassays

Toxicity:

With three exceptions, no direct toxic effects were demonstrated and results are not further illustrated.

Bioaccumulation of metals:

In *Limnodrilus sp.* very little metal accumulation occurred, probably partly due to relatively high metal concentration in the oligochaetes at the start of the exposure. The exception to this was mercury, which at least doubled in concentration after exposure to Sneepkil sediment and increased by a factor of 5 to 14 in oligochaetes exposed to samples from Gat van de Hengst. In *Lumbricus rubellus* on the other hand, a distinct accumulation was observed for all metals, except zinc. The zinc concentration appeared to be regulated as it ranged within a narrow bandwidth, despite the variation in zinc concentrations in the soil. Besides these differences between the two species, no significant differences in metal accumulation were observed within either *Limnodrilus sp.* exposed to sediment or *Lumbricus rubellus* in soil.

Table 2

Results from the bioaccumulation assays. Concentrations of metals and organic contaminants in *Limnodrilus sp.* and *Lumbricus rubellus* after 4 weeks of exposure. Concentrations are given as mg/kg dry wt (metals) or as mg/kg lipid (organic contaminants). Furthermore, concentrations at the start of the experiments are reported (t = 0).

Sampling location	Shallow water		Shallow water with reed		Intertidal mud flat		Reed vegetation		Marsh forest		t = 0
	S1	G1	S2	G2	S3	G3	S4	G4	S5	G5	100%
Limnodrilus sp.											
Metals (mg/kg dry wt)											
As	3.76	4.31	3.19	6.36	3.10	1.78					5.02
Cd	0.60	0.97	0.41	1.58	0.18	0.05					0.95
Cr	37.6	16.8	9.0	35.3	11.2	5.8					50.0
Cu	25.8	26.6	24.2	41.7	21.3	40.8					26.9
Pb	15.5	17.0	8.9	33.0	9.10	3.4					15.9
Ni	4.20	3.88	2.28	8.39	2.79	0.99					5.30
Zn	254	282	226	344	212	201					256
Hg	0.13	0.30	0.12	0.84	0.12	0.48					0.06
Organic contaminants (mg/kg lipid)											
Σ13 PAHs	38.3	43.6	30.1	38.7	24.6	23.4					16.1
Σ7 PCBs	7.6	8.4	6.5	8.8	5.6	6.9					5.6
p,p'-DDD	0.35	0.38	0.31	0.43	0.27	0.36					<0.09
Lumbricus rubellus											
Metals (mg/kg dry wt)											
As					2.29	1.64	1.66	2.34	1.14	1.84	0.56
Cd					6.17	6.16	7.87	12.40	10.70	9.72	3.80
Cr					49.4	27.0	44.0	37.9	21.3	19.4	12.7
Cu					19.0	15.2	16.7	20.0	15.3	18.3	11.7
Pb					10.6	7.4	7.9	13.1	6.2	8.9	3.4
Ni					4.64	2.99	3.40	3.62	2.31	3.52	1.39
Zn					1172	1127	1202	1142	1122	1097	1133
Hg					0.41	0.23	0.35	0.65	0.31	0.49	0.16
Organic contaminants (mg/kg lipid)											
Σ13 PAHs					4.1	2.1	2.6	3.6	2.4	2.9	3.0
Σ7 PCBs					2.1	1.8	1.7	8.5	1.9	1.6	4.0
Dieldrin					0.03	<LOD	0.03	0.03	0.04	0.04	<LOD

Bioaccumulation of organic contaminants:
In *Limnodrilus sp.* bioaccumulation of organic contaminants clearly occurred. The ΣPAH concentrations were between 1.5 and 2.7 times higher compared to the control samples at t = 0. Bioaccumulation was the highest in the aquatic sediments (S1 and G1), and the lowest at the intertidal mud flats (S3 and G3). The ΣPCB concentrations had also increased compared to the control, but no statistical significant differences were found along the gradient. For p,p'-DDD the concentrations increased by a factor of about seven, regardless of the origin of the samples along the gradients.

For *Lumbricus rubellus* a different pattern emerged, since both ΣPAH and ΣPCB concentrations were highest in the control samples at t = 0. The low background levels in *Lumbricus rubellus* (as compared to *Limnodrilus sp.*) remained the same or even decreased when exposed to samples from the intertidal mud flats.

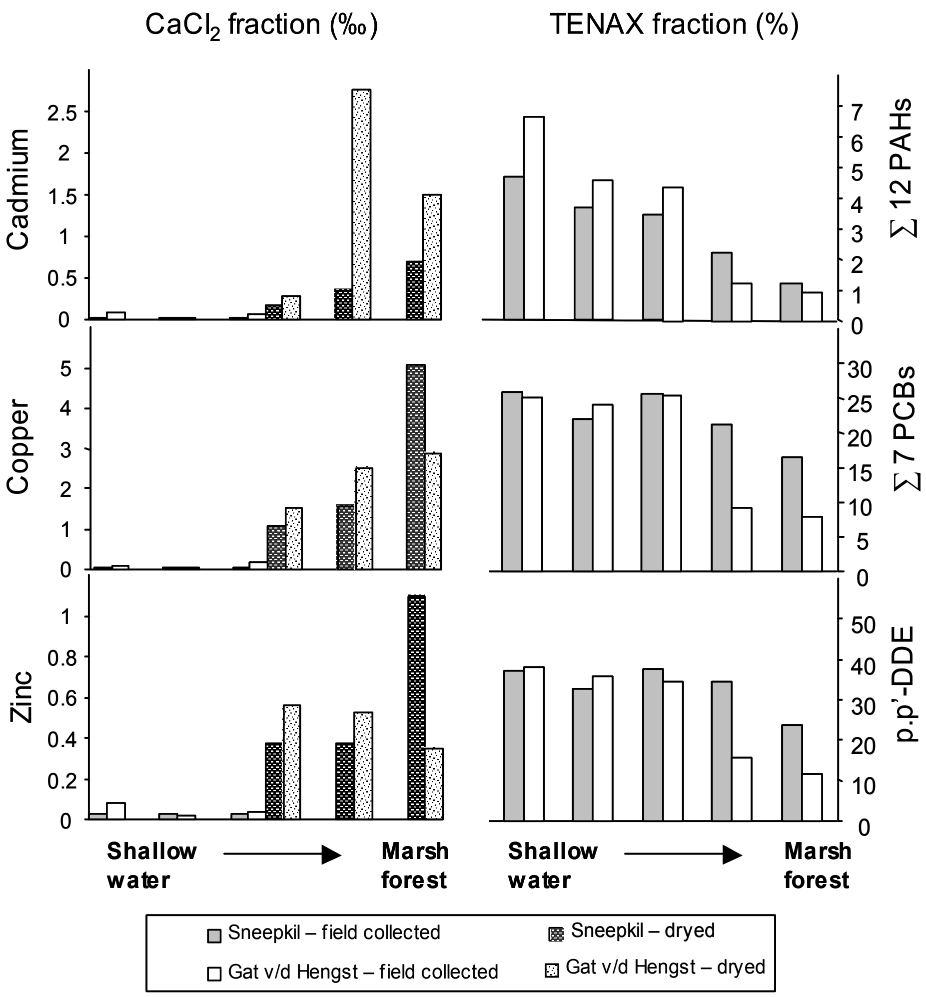

Figure 1: $CaCl_2$-extractable fractions of cadmium, copper and zinc in field collected or dried sediment and soil samples as well as Tenax extractable PAH, PCB and p,p'-DDE fractions in field collected samples along the gradients from shallow water to marsh forest.

4 Discussion

The results from the chemical analyses and the bioassays were in line with a previous study in this area (DEN BESTEN et al. 2000), concluding that indirect effects caused by secondary poisoning were more important than direct effects posed upon sediment and soil fauna. As compared to direct effects, more distinct differences in relation to the gradients were observed in the bioavailability and the accumulation of the contaminants between the aquatic and terrestrial samples. The assessment of the ecological risks was therefore narrowed down to these findings.

4.1 Location specific assessment

A clear difference was observed in the bioaccumulation of metals between aquatic and terrestrial assays. With *Limnodrilus sp.* very little accumulation of metals occurred, whereas *Lumbricus rubellus* accumulated significant amounts of metals. This difference was especially clear in the intertidal mud flats, which were tested using both organisms. Even though metal natural background levels were higher in aquatic *Limnodrilus sp.*, the terrestrial *Lumbricus rubellus* had accumulated metals at the end of the exposure period to levels above those found in *Limnodrilus sp.* This might partly be due to species-specific differences towards metal accumulation, but bioaccumulation differences can nonetheless also be expected due to differences in metal availability between aquatic and terrestrial sediments. For instance, the higher $CaCl_2$-fraction of Cd in the terrestrial samples corresponds with an increased bioaccumulation of Cd in *Lumbricus rubellus*. An improvement in the correlation between cadmium concentrations in soil samples versus internal cadmium concentrations in the organisms is noted if $CaCl_2$-extractable fractions are used instead off total cadmium concentrations (Figure 2).

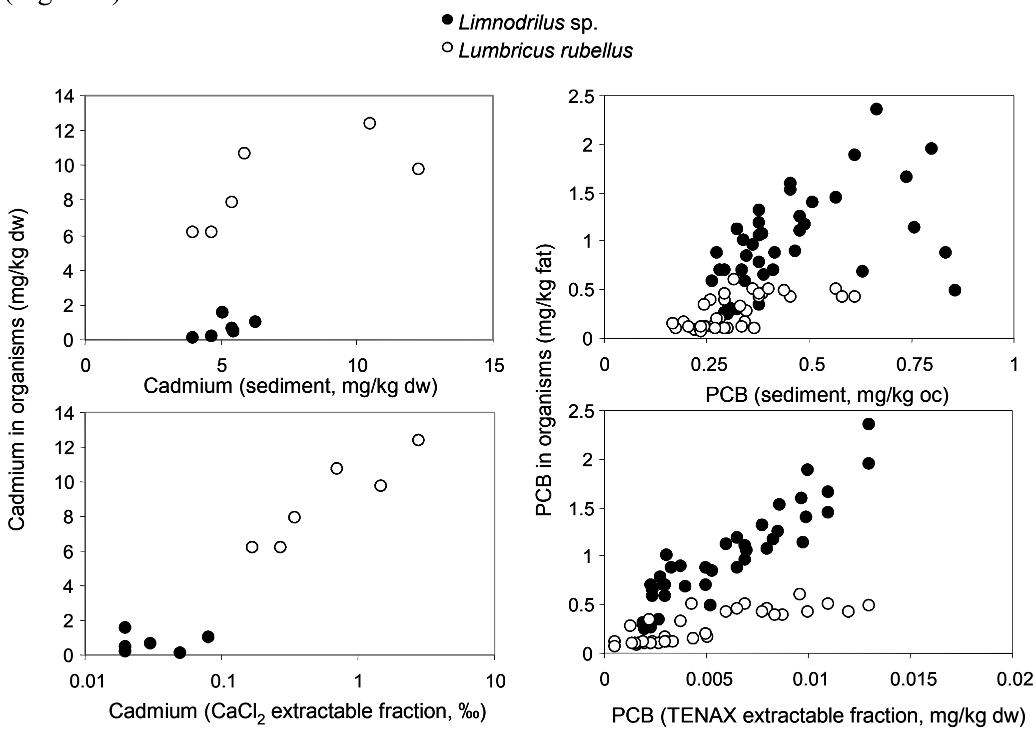

Figure 2: Internal cadmium and PCB concentrations in the aquatic *Limnodrilus sp.* (●) and the terrestrial *Lumbricus rubellus* (○). Concentrations are related to either the total concentrations in the sediment and soil (top graphs) or the bioavailable fraction (bottom graphs).

The bioaccumulation patterns of organic contaminants (Table 2) were reversed to those observed for metals. Concentrations of PAHs and PCBs in *Limnodrilus sp.* increased during the exposure period, while remaining constant in *Lumbricus rubellus*. A further illustration of this pattern was found in a direct comparison between the two species exposed to samples from the intertidal mud flats. The low background levels of PAHs and PCBs in *Lumbricus rubellus* remained low, or even decreased further, while these levels in *Limnodrilus sp.* increased during exposure to the same sediments. As illustrated in figure 2, a large portion of the variation in internal PCB concentrations could not be explained by standardizing concentrations in sediment and soil on organic carbon content. Besides total carbon content, the quality and constitution of the organic matter will also influence the availability of organic contaminants (GARBARINI & LION 1986; GUNNARSON et al. 1999; RUTHERFORD et al. 1992). Especially in the case of aquatic-terrestrial gradients, this may play an important role, since for example the source of the organic matter in sediment differs from that in the soil. Bioavailability measurements, like Tenax extractions, might therefore show an improved correlation with internal PCB concentrations (Figure 2). From this figure, it is clear that a good correlation existed between accumulated PCB and Tenax extractable fractions. This relationship based on Tenax extractable fractions is further described and discussed by TEN HULSCHER et al. (2003). In view of these findings, Tenax extraction appeared to be a proficient tool for the assessment of bioavailability of organic contaminants in sediments and soils. Still, a species-specific difference seemed to be present since the relation between the Tenax extractable PCB fraction and the internal concentration in the organisms (mg/kg fat) differed between *Limnodrilus sp.* and *Lumbricus rubellus*. As indicated above, species-specific differences might be responsible for this difference (e. g. SCHULER et al. 2003). Another explanation may also be possible. In contrast to $CaCl_2$-extractions, Tenax extractable fractions were only analyzed in field collected samples. The terrestrial samples, which were additionally dried prior to the start of the experiments, were not analyzed after drying. As the availability of organic contaminants in terrestrial samples was already low compared to aquatic samples, additional drying might have further decreased availability.

In contrast to the differences between aquatic and terrestrial locations as discussed above, differences among the results obtained by the aquatic bioassays and bioaccumulation experiments on the three different locations (shallow water – intertidal mud flat) were of minor relevance. The same applies to the results obtained by the terrestrial experiments on the three different locations (intertidal mud flat – marsh forest). It is therefore concluded that it does not seem necessary to make distinction between all locations along a gradient. A distinction between either aquatic or terrestrial locations may be sufficient for ecological risks assessments. Intertidal mudflats, being alternately aquatic and terrestrial, resembled more closely aquatic locations based on chemical measurements immediately after sampling ($CaCl_2$ or Tenax). However, they seemed to adapt quite fast to changing circumstances. Cadmium, copper and zinc concentrations sharply increased in $CaCl_2$-extractions following the drying of samples (ZHANG et al. 2001).

4.2 Integration of aquatic and terrestrial risk assessment

This study aimed at testing a scheme for an integrated assessment of aquatic sediments, flood plains as well as terrestrial ecosystems. Considering the results it is clear that sediments and soils from neighbouring aquatic and terrestrial systems may render different assessments in terms of environmental risks. In aquatic environments, metal availabilities for oligochaetes appeared to be limited, whereas organic contaminants (PAHs and PCBs) were bioavailable. In the terrestrial environment the opposite was observed: Metals were more bioavailable and organic contaminants were less bioavailable. The use of $CaCl_2$- and Tenax-extraction to describe availability have led to a better understanding of these differences along the gradient. Consequently, such a comparison of environmental risks associated with contaminated sediments and soils along a gradient of aquatic and terrestrial conditions provides useful information when considering (prioritisation of) remedial actions in areas where both aquatic and terrestrial systems exist in close proximity.

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Sediment contact tests as part of a holistic approach. Part: Nematodes

Sebastian Höss

Zusammenfassung

Um das Risko anthropogener Verschmutzung für Ökosysteme bewerten zu können, ist es notwendig alle Organisations- und ökologischen Niveaus zu berüchsichtigen, vom ganzen Organismus zum Genom, von der einzelnen Art zum komplexen Nahrungsnetz. Deswegen müssen Single-Species-Tests von Methoden begleitet werden, die es ermöglichen, Effekte auf der molekularen und Community-Ebene zu bewerten. Neben ihrer hohen ökologischen Relevanz für benthische Habitate sind die Nematoden eine geeignete Organismengruppe, um ökotoxikologische Effekte auf allen Organisations- und ökologischen Niveaus zu untersuchen. Während *C. elegans* ein ausgezeichneter Modellorganismus für Single-Species Toxizitätstests (vor allem Sedimentkontaktests) und molekulare Studien ist, bietet die gesamte Gruppe der Nematoden mit hohen Abundanzen und hoher struktureller und funktioneller Diversität gute Voraussetzungen für die Untersuchung von Wirkungen auf Lebensgemeinschaften und Nahrungsnetze.

Summary

To assess the risk of anthropogenic pollution for ecosystems it is necessary to consider all organizational and ecological levels, from whole organisms to the genome, from single species to complex food webs. Thus, single-species toxicity tests have to be accompanied by methods that allow to assess effects on molecular, as well as on community level. Besides their ecological relevance for benthic habitats, nematodes are a suitable organism group for studying ecotoxicological effects on all organizational and ecological levels. While *C. elegans* is an excellent model organism for single species toxicity tests (i. e. sediment contact tests) and molecular studies, the whole group of nematodes offer with high abundances and high structural and functional diversity good requirements for studying effects on community and food web level.

To assess the risk of anthropogenic chemical on ecosystems, it is not sufficient to measure environmental concentrations. To consider the interaction with the living environment (biota), it is necessary to study effects of the chemicals on organisms. This can be done on various levels: Single species bioassays can be used to get information on the toxicity of single compounds, chemical mixtures or environmental samples on whole organisms. By using ecologically relevant toxicity endpoints, such as reproduction, effects can even be assessed on population level. Realistic exposure scenarios, as given for sediment contact tests, allow a better interpretation of toxicity data, in terms of bioavailability of contaminants. This is particularly important when regarding complex test matrices, such as aquatic sediments. However, single species tests have their limits and for a holistic risk assessment additional approaches have to by applied. The limits lie (1) in the expolation of single-species toxicity data to higher ecological levels, such as communities or food webs, (2) in the identification of mode of actions of single compounds, and (3) the indentifications of cause-effect relationships in multi stress situations. Thus effects have also to be assessed on community level, to address e. g. also indirect food web effects, as well as on sub-organismic or even molecular level to unravel the mode of action of certain chemicals. Moreover, sophisticated chemical methods (e. g. biomimetic extraction methods; fractionation) have to be combined with bioassays to get information on the causality of toxic effects in sediments (e. g. EDA).

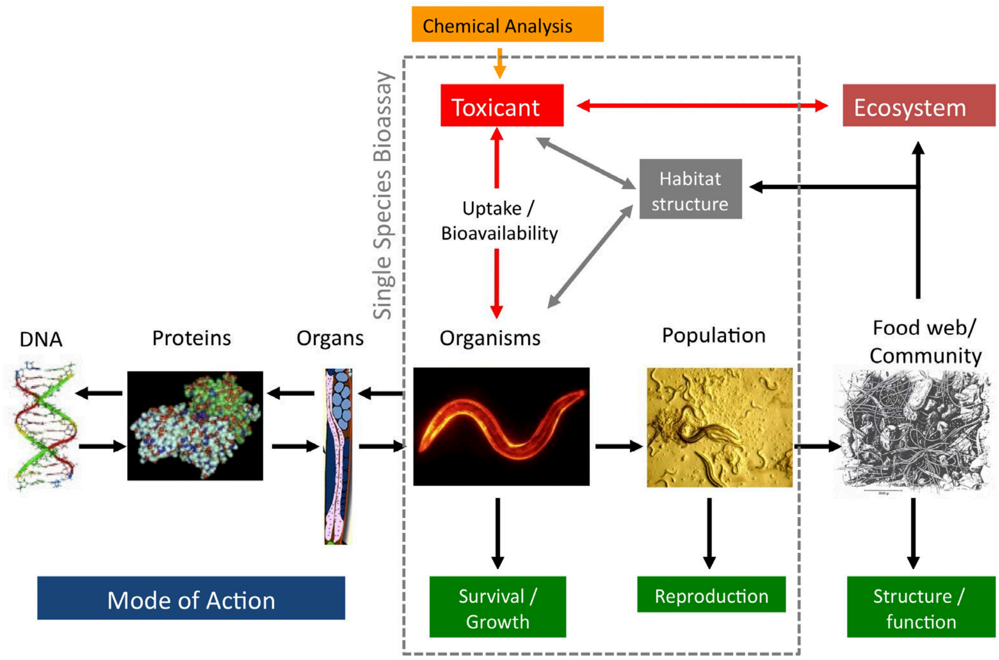

Figure 1: The role of single species bioassays for an environmental risk assessment of toxicants.

All these methods, that can be used for an integrative environmental risk assessment require different experimental setups or study dimensions, ranging from in vitro tests to field studies (Figure 2). As each single method can always be a compromise between interpretability on one hand and ecological relevance on the other hand, a combined approach, such as the sediment quality triad is necessary (CHAPMAN 1990).

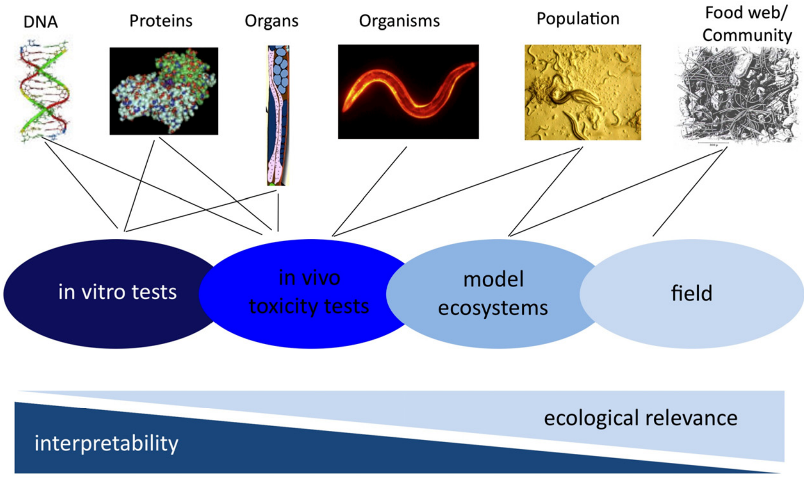

Figure 2: Classifications of ecotoxicological units in terms of ecological level, study demension, interpretability and ecological relevance.

Nematodes are often the most abundant and species richest metazoans in aquatic sediments. As they evolved various feeding strategies (bacteria, algae, fungi and plant feeders, omnivors, predators), nematodes play an important role in benthic food webs (Figure 3). Besides their ecological relevance, nematodes are suitable bioindicators for all ecotoxicological tools, from molecular to community level. In the following, some examples are shown, to demonstrate the usefulness of this organism group for an environmental risk assessment, at all organizational and ecological levels (Figure 1).

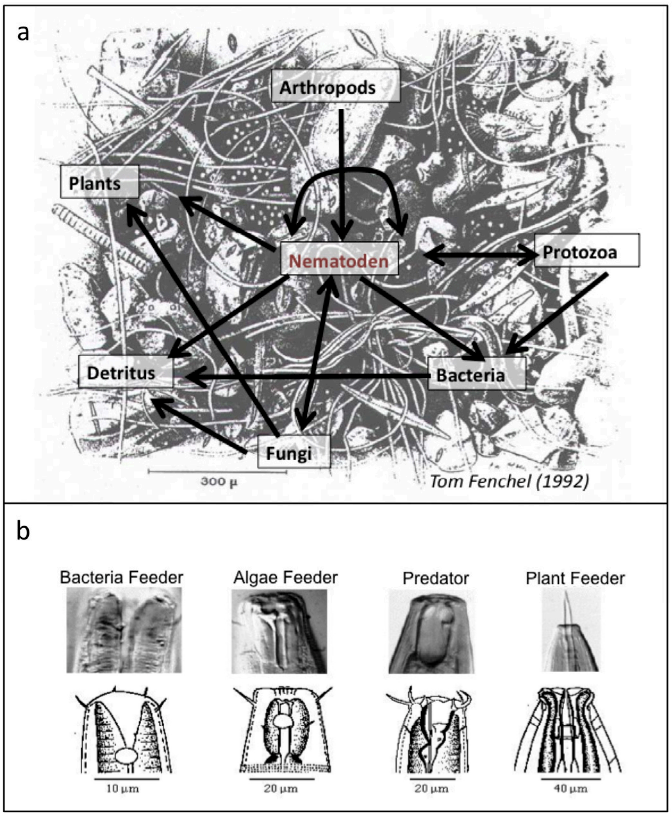

Figure 3:
a) Role of nematodes in bentic food webs (background picture taken from FENCHEL (1992));
b) Various feeding types evolved by nematodes (fotographs and drawing of the buccal cavities of some nematode species; provided by Prof. Dr. Walter Traunspurger, University of Bielefeld)

For single-species toxicity tests commonly only few representative species are chosen for establishing a standardized test protocol. In case of the nematodes, the bacterial feeder, *Caenorhabditis elegans,* was proposed as ecotoxicological test organisms, as it is easy to culture, has a short generation time, is one of the best studied multi-cellular organisms, and can be maintained in various media. Thus, already two standardized test protocols exist, for testing water, sediment and soil (ASTM 2001, ISO 2008). In the SeKT research project, the nematode contact test (ISO/CD 10872) turned out to be a suitable test organism within the suggested test battery (FEILER et al. 2008). When extending the test duration to approx. 30 day, a whole life cycle can be observed, allowing for assessing effects on total brood size or life span (e. g. PETRASCHECK et al. 2007).

Adverse effects on nematodes can also be shown on sub-organismic level. As nematodes are transparent, damages on organs can easily be observed by light microscopy. Germs cells, for example, can be stained with DAPI, and counted as a parameter of endocrine disruption in the nematodes (HOSHI et al. 2003). As another example, WEI et al. (2003) could show gut damages to the gut of *C. elegans* that were induced by crystal proteins, toxins produced by the soil bacterium *Bacillus thuringiensis* (*Bt*-toxins). Moreover, it could be shown, that fluorescence labeled toxins were able to bind to the gut surface of *C. elegans* (HUFFMAN et al. 2004b). These observation indicated that the mode of action of *Bt*-toxins in nematodes is similar to that in insects.

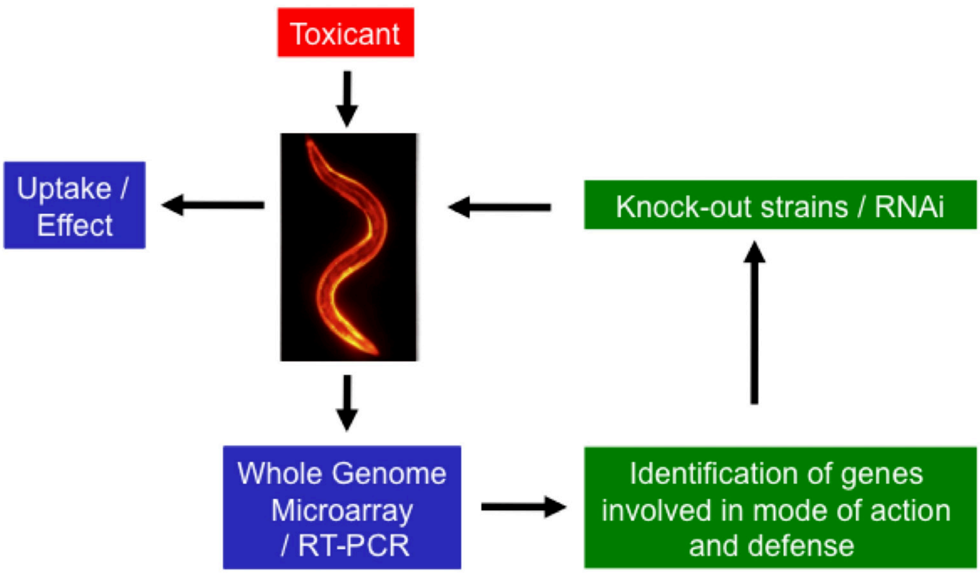

Figure 4: Approach to unravel modes of action using molecular techniques.

To learn more about the mode of action of a toxicant it is helpful to look at the molecular level (Figure 4). *C. elegans* is a useful model organism for molecular studies, as it is one of the best investigated organisms. It is possible to identify genes that are induced by a certain stressor by assessing the gene expression pattern using a whole DNA microarray (KIM et al. 2001). Using RT-PCR (reverse transcriptase polymerase chain reaction), the effect of a toxicant on the regulation of the gene of interest can then be quantified. To verify, if the identified gene is (at least partly) responsible for a certain toxicity pathway, mutant strains, where specific genes had been knocked out, are tested for the sensitivity towards the toxicant. Alternatively, genes can be silenced using RNA interference (RNAi). As an example, HUFFMAN et al. (2004a) identified genes and pathways that are involved in the defense mechanism of *C. elegans* against crystal proteins (*Bt*-toxins). Knock-out strains of *C. elegans*, missing these genes, were hypersensitive towards the toxins, but not towards other toxicants, such as cadmium.

Molecular methods might not only be interesting for the elucidation of toxicity pathways, but also might be used for a toxicity identification evaluation (TIE) in complex mixtures. However, to use gene expression as an ecotoxicological endpoint or a tool for TIE in sediment toxicity assessment there is still requires a lot of basic research. Nevertheless, there are first attempts showing that it is possible to distinguish different gene expression patterns in *C. elegans* when exposing the organisms to whole sediment samples with different qualities and quantities of contamination (MENZEL et al., under review).

Besides the high value of the well-investigated model organism *C. elegans*, nematodes are also suitable bioindicators at the community level. The high abundances, as well as high structural and functional diversity of nematodes in benthic habitats allow on one hand a statistically valid community analysis also in relatively small samples, on the other hand, indirect effects can be detected with changes in the nematode community structure, due to their multiple involvements in the benthic food web. For terrestrial ecosystems, a “stress index”, the Maturity Index, was developed, that categorizes the nematodes according to their reproductive strategy. Also for freshwater sediments, the nematode community structure was found to be related to the degree of pollution (BARBUTO & ZULLINI 2005, HEININGER et al. 2007).

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Sediment contact assay with fish egg as part of a holistic approach to sediment risk assessment

Henner Hollert, Thomas-Benjamin Seiler and Arnold V. Hallare

Zusammenfassung

Die verbesserte Umweltqualität von Oberflächengewässern und –sedimenten erfordert umfassende Strategien für eine ökotoxikologische Bewertung. Während in der Bundesrepublik Untersuchungsstrategien auf der Basis von chemischen Analysen und der akuten Toxizität in den letzten Jahren dominierten, ist heutzutage die Untersuchung des bioverfügbaren Anteils der Sedimenttoxizität (Sedimentkontakttests) und Mechanismus-spezifischer Biotests in der Ökotoxikologie notwendig, um den guten chemischen und ökologischen Zustand von Oberflächengewässern zu erreichen, den die EU-Wasserrahmenrichtlinie für europäische Flussgebiete bis 2015 fordert. Sedimente sind seit langem als Senke und Quelle von Schadstoffen in aquatischen Systemen bekannt. In vielen Fällen konnte für Partikel-gebundene Schadstoffe eine embryotoxische und teratogene Wirksamkeit in aquatischen Organismen nachgewiesen werden, insbesondere in Fischen. Daher besteht eine große Notwendigkeit, wirbeltiernahe Testsysteme zur Überprüfung der Embryotoxizität zu entwickeln, zu standardisieren und in aktuelle Sedimentbewertungsstrategien zu integrieren. Dieser Beitrag führt in verschiedene Konzepte ein, mit denen das ökotoxikologische Schädigungspotenzial in deutschen Flüssen identifiziert wird. Es besteht weitgehend Konsens, dass Sedimentkontakttests das geeignetste Szenario darstellen, um *in-situ*-Exposition zu simulieren. Sedimentkontakttests können als zusätzliche Beweislinie in *Weight-of-Evidence*-Studien genutzt werden, um den Anteil der bioverfügbaren Fraktion der toxischen Sedimentwirkungen zu identifizieren.

Zunächst wird in dem Beitrag die Eignung des Sedimentkontakttests mit *Danio rerio* vorgestellt, Oberflächen- und Bohrkernproben des Neckars und der Donau ökotoxikologisch zu bewerten. Zahlreiche Endpunkte, auch solche zur Genotoxizität, können in wirbeltiernahen Testsystemen bisher nur nach dem Transfer in die wässrige Phase untersucht werden. Kürzlich wurde allerdings ein Sedimentkontakttest mit Zellen von *Danio rerio*-Embryonen entwickelt, mit dem nach Sedimentkontaktexposition der Anteil der bioverfügbaren Gentoxizität von Sedimenten ermittelt werden kann. Dies zeigt das enorme Potenzial des Fischei-Sedimentkontakttests für die Risikobewertung belasteter Sedimente und bildet sicherlich nur den Auftakt für eine ganze Reihe zukünftiger Entwicklung hinsichtlich intergrierter Untersuchungsstrategien in der Sedimenttoxikologie.

Summary

Improved quality of surface waters and sediments requires advanced strategies for ecotoxicological assessment. Whilst at least in Germany assessment strategies on the basis of chemical analysis and acute toxicity data alone dominated the last decades, the investigation of the bioavailable fraction of the sediment toxicity (through sediment contact assays) in combination with more specific biological endpoints in ecotoxicology is necessary in order to achieve a good ecological and chemical status of surface waters in the European river basins until the year 2015, as mandated by the European Water Framework Directive. Sediments for long have been known to function both as a sink and a source of pollutants in aquatic systems. In addition, part of the particle-associated substances has frequently been demonstrated to cause embryotoxic as well as teratogenic effects in aquatic organisms and particularly in fish. Hence, there is – among other requirements – an urgent need to develop, standardize and implement integrated vertebrate-based test systems addressing embryotoxicity within recent sediment investigation strategies. The present communication introduces different conceptual frameworks for identifying the hazard of sediments in German rivers. There is a broad consensus that whole-sediment exposure protocols provide the most realistic scenario to simulate *in situ* exposure conditions. Sediment contact assays can be used as additional lines of evidence in Weight-of-Evidence approaches to give insight into the bioavailable toxicant fraction.

First of all, the suitability of the fish egg contact assay with *Danio rerio* is shown for the evaluation of the ecotoxicological burden of surface and core sediment samples from the rivers Neckar and Danube. However, several endpoints including genotoxicity in vertebrate-based systems could only be tested after transferring the particle-bound substances into the aqueous phase. Recently, a sediment contact assay with cells from early-stage *Danio rerio* embryos for the evaluation of the bioavailable fraction of the total genotoxic hazard potential of sediments has been developed. Surely, a lot of possible research ideas and undertakings will come out in the future highlighting the immense potential of the fish egg sediment contact assay with *Danio rerio* in sediment toxicology and risk assessment.

1 The need for sediment risk assessment

The sediment is considered as an essential, integral, and dynamic part of our aquatic systems. It provides breeding grounds as well as nutrient sources for many organisms while its dynamics and gradients form favorable conditions to support biodiversity. However, many of the sediments in our rivers, lakes, estuaries, and coastal zones have already been contaminated by pollutants. Contaminated sediments have been created by decades of municipal and industrial discharges, combined sewer overflows, and agricultural, non-point source runoff. Various contaminants may have also been carried through the air, landing in lakes, and streams and ultimately end up in sediments. Buried contaminants posing serious human and ecological health concerns can be remobilized during storm and flood events (HOLLERT et al. 2000), through dredging and relocation of sediments (KÖTHE 2003), via bioturbation (POWER & CHAPMAN 1992) and feeding activities of bottom-dwelling organisms. Many of these small bottom-dwellers ingest toxins as they feed on the sediments. As they are eaten by their larger consumers, the toxins move up the food chain, their concentrations getting higher, often thousands of times higher. Thus, once sediments are contaminated, they may act both as sink and as secondary sources for many persistent, potentially toxic chemicals (BETTINETTI et al. 2003, HOLLERT et al. 2003).

Contaminated sediments first began to be noticed as a serious environmental problem in the early 1970s when increases in the concentrations of the pesticide DDT and a group of chemicals known as polychlorinated biphenyls (PCBs) were detected in the tissues of Great Lakes fish (DELFINO 1979). Because the number of sites around the world with contaminated sediments steadily increases at an alarming rate, efforts and initiatives were made to present sediment contamination as a significant global and regulatory issue (HARKEY et al. 1994). Since then, various agencies for environmental protection have made it obligatory to expand water quality monitoring via inclusion of sediment risk assessment (TRAUNSPURGER et al. 1997, AHLF et al. 2002, USEPA 2001, USEPA 2002). In a report on SedNet Round Table discussion in 2006, European scientists have also recognized the role played by incorporating sediments to reach the good ecological and chemical status for four European river basins by the year 2015, as mandated by the Water Framework Directive (NETZBAND et al. 2007).

2 Conceptual approaches in sediment risk assessment

2.1 From chemical analysis to bioassays to Sediment Quality Triad (SQT)

In response to the emerging issue on global sediment contamination and in order to protect the aquatic life community, comprehensive methods and approaches for identifying and assessing the severity of sediment contamination have been developed since the early 1970s (Figure 1). The very first approach was to merely employ chemical analyses. Though it is a highly effective analytical tool that is capable of detecting both source substances and their metabolites, the chemical analysis approach fails to provide information on the actual bioavailability and biological activities of the toxicants. No information concerning synergistic/ antagonistic potential in sediments is likewise provided by chemical data. The presence of millions of chemicals in waters and sediments also prevents any complete chemical screening to be done due to time, effort, and cost considerations. About a decade later, a battery of *in vitro* bioassays was developed and adapted for the evaluation of sediments, soils, and suspended particulate matter. In order to ensure that the actual bioavailability of sediment contaminants is sufficiently considered, efforts were done to conduct bioassays using sediment contact tests in different exposure scenarios. However, since sediment contact assays with whole organism usually provide only acute (mortality) and chronic toxicity data, it has become necessary to subject the test organisms after exposure to more specific mechanism-based bioassays (e. g. mutagenic, genotoxic, teratogenic, dioxin-like, and estrogen-like responses, HOLLERT et al. 2009). In this way, we can gain a more comprehensive insight into the potential ecotoxicological hazard of sediments.

For the evaluation of aquatic sediments with respect to their adverse effects on ecosystems, however, neither biotests nor chemical-analytical techniques alone are sufficient. Thus, a need for more integrated and hierarchical approaches combining chemical, ecotoxicological, and ecological information has been proposed (AHLF et al. 2002, BURTON 1991, CHAPMAN

2000, HEISE & AHLF 2002). As a consequence, CHAPMAN (1990) introduced the Sediment Quality Triad (SQT) approach which simultaneously investigates sediment chemistry, sediment toxicity, and sediment ecology (alterations in the field e. g. modifications of benthic community structure). Assessments of these three areas are integrated to reach conclusions based on the degree of risk indicated by each measurement and the confidence in each measurement. These three lines of evidence serve as the original components of the SQT. In the context of ecological risk assessment (ERA) of contaminated sediments, the SQT provides a Weight-of-Evidence (WOE) framework (CHAPMAN 2000) comprising a determination related to possible ecological impacts based on multiple lines of evidence (LOE).

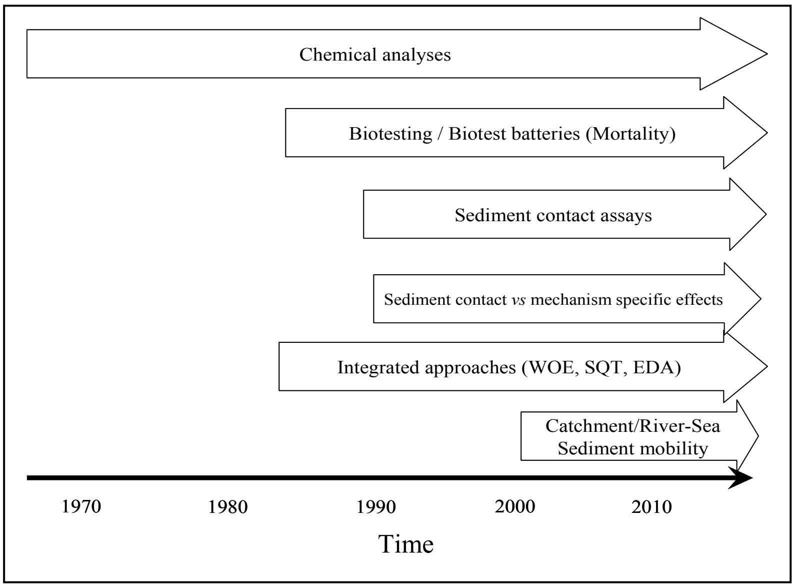

Figure 1: Historical development of the various approaches in sediment risk assessment.

2.2 Expansion of SQT through additional LOEs

The SQT provides the basis for contaminated risk assessment (SUTER 1996) and as originally conceived by CHAPMAN (1990), was never intended to be limited to only three specific LOEs. CHAPMAN & HOLLERT (2006) provided recommendations regarding the expansion of the original SQT to include additional LOEs. These additions will provide better alternatives available for the weight of evidence framework. A total of 14 LOEs as replacements or additions to the alterations to resident communities LOE was proposed and applied. The choice of specific LOE will depend on several factors such as site conditions, reference conditions, stressors of potential concerns, and receptors of potential concerns. For example, one of the most promising additional lines of evidence is the information derived through the use of effect directed analysis (EDA). EDA supplements the SQT by putting a solving extension to it with respect to the key toxicants involved in the toxicological effect assessment. It is based on a combination of fractionation procedures, biotesting, and chemical analytical methods (BRACK 2003). EDAs sequentially reduce the complexity of an organic sediment extract by removing nontoxic components in order to enable a chemical identification of the remaining toxicants. Management and mitigation efforts will then be focused on the toxicants identified through the EDA (BRACK et al. 2005).

Other approaches and new concepts will be added to incorporate impending issues affecting sediment risk assessment. These include sea level rise brought about by global climate change, dredging activities, and flooding and how these factors can influence sediment mobility and contaminant transport patterns in the future.

3 Different exposure pathways of sediment contamination

One important consideration in sediment risk assessment is the recognition that the sediment itself serves as a secondary contaminant source. This poses a threat to organisms in which sediments serve as habitat and food source, and might become an obstacle for implementing the Water Framework Directive (FÖRSTNER 2002). Efforts are then directed towards understanding the different possible pathways in which organisms can be exposed to the contaminants. Bioavailability of sediment contaminants should be addressed sufficiently in any toxicity assays. The question as to which should be used as the test phase became the most important issue in sediment toxicity testing protocols. Test phases can be categorized as follows: (a) organically extractable phases (in solvents other than water), (b) elutriate phase (water-extractable), (c) interstitial water phase (pore water), (d) whole sediment, and (e) *in situ* assays (BURTON 1991). There is a broad consensus that the whole sediment exposure protocols represent the most realistic scenario to stimulate *in situ* exposure conditions in the laboratory (cf, HOLLERT et al. 2003, HARKEY et al. 1994). Nevertheless, organic extracts of whole sediments have frequently been used to assess the potential ecotoxicological burden of sediments and in situations that require identification of soluble toxicants via toxicity identification evaluation. Elutriate fractions, although originally intended to mimic the open-water disposal of dredged materials and flood events, have also been used to determine the toxicity of contaminated sediments.

4 Various ecotoxicological (mechanism-based) endpoints in sediment assessment

Contaminated sediments, to which organisms are exposed, contain toxicants of various structural complexities and wide array of biological activities. Different chemicals will utilize specific biochemical and cellular pathways to manifest their own mode of action to induce toxicological effects (for review: HOLLERT et al. 2009). Some substances can directly target the DNA structure causing genotoxic damage that can result in increased risk towards development of diseases. Other substances, called endocrine disrupting chemicals, can mimic or interfere with the normal functioning of hormones and disrupt normal reproductive development and endocrine functions of wildlife. Still, other substances in sediments could have dioxin-like activities, wherein they bind to the aryl hydrocarbon receptor (AhR) and provoke transcription of genes for several cytochrome P450 (CYP) enzymes. These enzymes metabolize the contaminants to reactive intermediates that may induce a wide spectrum of toxic and biochemical effects including embryotoxicity, teratogenicity, hepatotoxicity, immunotoxicity, dermal toxicity, lethality, carcinogenesis, wasting syndrome, and tumor promotion in many species even at low concentrations. Still other substances target cellular proteins that play critical roles during development. Organisms respond to such cellular phenomenon by increasing the transcription of stress protein genes (stress protein response), the products of which (heat shock proteins) are utilized immediately in repairing partly denatured and malfolded proteins as well as in inhibiting the formation of insoluble and damaging aggregates. All of these various toxicological endpoints, if not repaired, can trigger a cascade of biological consequences at the cellular, organ, whole organism, and finally population and community levels.

Different exposure pathways can establish which contaminants become bioavailable and can dictate which specific 'mechanism-based' endpoints will be elicited in exposed organisms. As mentioned earlier, whole sediment exposure aptly represents the most realistic scenario and therefore, an assay which takes this into account provides the best indication of the ecotoxicological hazard of sediments.

5 The need for sediment contact test

Despite the fact that whole sediment exposure represents the actual bioavailability of sediment contaminants, previous sediment toxicity biotests had utilized other phases for exposing test organisms. Through the years, there have been efforts to develop various sediment contact assays with the intention of determining the effects caused by whole sediments, and at the same time taking into account all possible pathways of contaminant uptake by the test organisms (particle contact, food, pore water) (FEILER et al. 2005). In sediment contact test approach, effort is ensured that intact organisms or *in vitro* systems are exposed to contaminants borne from sediments. In designing a battery of contact assays, prime consideration is given to its capability to represent all trophic levels. Conventionally, sediment contact screening assays have been conducted to include only the (a) primary producers (e. g. algal growth inhibition test – DIN 38412 L33, 1991), (b) prokaryotic organisms (e. g. bacterial contact assay with whole sediments – DIN 38412 L48, 2002 and Microtox assay with *Vibrio fischeri* – DIN 38412 L37, 1997), and (c) invertebrates (e. g. *Daphnia magna* –DIN 38412-L30,1987) as well as chironomids, midges, crabs, oligochaete, polychaete, mussels, oysters, sea urchins and sand dollars, reviewed by INGERSOLL et al. 1995). In previous studies, it was concluded that a bioassay battery that is based only on primary producers, degraders, and invertebrates could not provide a good estimation of the total ecological hazard potential of sediments (AHLF et al. 2002, HOLLERT 2001, HOLLERT et al. 2002, ULRICH et al. 2002). Consequently, these studies suggested a need to develop, standardize, and implement a sediment contact assay using vertebrate-based test systems.

The suitability of using adult vertebrate fish for sediment contact tests has been similarly subjected for intensive evaluation. This is because adult fish and other pelagic vertebrates were rated as less suitable for sediment toxicity testing since they are not in direct contact with the sediment (USEPA 1994, ASTM 1995). Many pelagic and epibenthic organisms, however, depend on sediments as food source and breeding substrate so that effects on reproductive behavior, embryo development hatchability, and growth are critical and interesting endpoints to monitor (BURTON 1991). Accordingly, we have developed a new sediment contact assay that makes use of zebrafish eggs which are allowed to develop on the surface of the sediment, i. e. in direct contact with it and its contaminants (HOLLERT et al. 2003). The corresponding embryotoxicity and teratogenicity parameters induced by the sediment-borne contaminants are then monitored at specific developmental stages and time points.

Recently, other sediment contact tests were introduced and validated using bacteria – *Arthrobacter globoformis (*NEUMANN-HENSEL et al. 2006, RÖNNPAGEL et al. 1998), yeast – *Saccharomyces cerevesiae* (WEBER et al. 2006), nematodes – *Caenorhabditis elegans* (TRAUNSPURGER et al. 1997), oligochaetes, and higher plants – *Myriophyllum aquaticum* (FEILER et al. 2004). In order to compare the newly-developed sediment contact assays in terms of reference conditions, control sediments, and toxicity thresholds, and improve their applicability for sediment quality assessment, a German BMBF-funded joint project called SeKT (German: SedimentKontaktTests, FEILER et al. 2005) was undertaken and was successfully brought to completion in 2008.

6 The Fish Egg Assay as a novel sediment contact test

6.1 Description

The sediment contact assay using zebrafish egg (HOLLERT et al. 2003) is an offshoot of the original zebrafish embryo assay (DIN 38415-T6, 2001), which is a widely-used bioassay system for the analysis of single, pure chemicals and environmental samples (NAGEL 2002, BRAUNBECK et al. 2005). Since experiments with embryos are considered as alternative to animal experiments, the zebrafish embryo assay has the advantage of not being subject to either ethical issues or regulation by the current European Union legislation for the protection of animals used for experimental and other scientific purposes (Commission of the European Communities, 1986). Starting in 2005, the assay has become a mandatory component in routine whole effluent testing in Germany. Furthermore, the zebrafish embryo assay has also been subjected to standardization at the international level (EN ISO and OECD guidelines, 1996 a,b,c, 1998, 2007). Upon spawning, the zebrafish eggs sink straight to the bottom surface and come into direct contact with the sediments and possible contaminants. That is why this method was conceived to offer the most realistic scenario concerning bioavailability of chemicals in field situations. Initial studies that made use of sediment contact test with zebrafish eggs to monitor toxic effects of native sediments on a microtiter scale have only been published quite recently (HOLLERT et al. 2003, HALLARE et al. 2005, KEITER et al. 2006).

6.2 Methodology

The complete procedure for testing whole sediments with zebrafish embryos, including information on test species, fish maintenance, spawning procedure, test concentrations and controls, toxicological endpoints, and data collection and analysis, is given elsewhere (cf, HOLLERT et al. 2003, BRAUNBECK et al. 2005). Briefly, fertilized zebrafish eggs (4 to 32 cell stages) are exposed to different concentrations of the whole dry sediment samples in 6-well microtiter plates (cf, Figure 2). Three wells on the plate are allotted for each concentration and each well contains 3 g of sediment per 5 ml of artificial ISO water that is previously aerated to oxygen saturation. Each well contains 5 fish eggs. Two negative controls are used: a water control and a sediment control. A total of 20 eggs for each of the controls is used. The 3,7 mg/L DCA solution is used as positive control and to this 10 eggs are exposed. All the embryos are observed after 24 and 48 hours under the microscope. Oxygen concentrations are checked after 48 hours. The toxicological endpoints used to determine the lethality in embryos and larvae are given in BRAUNBECK et al. (2005) and DIN 38415-T6: egg coagulation, non-development of somites, tail not detached from yolk, no recognizable heart beat.

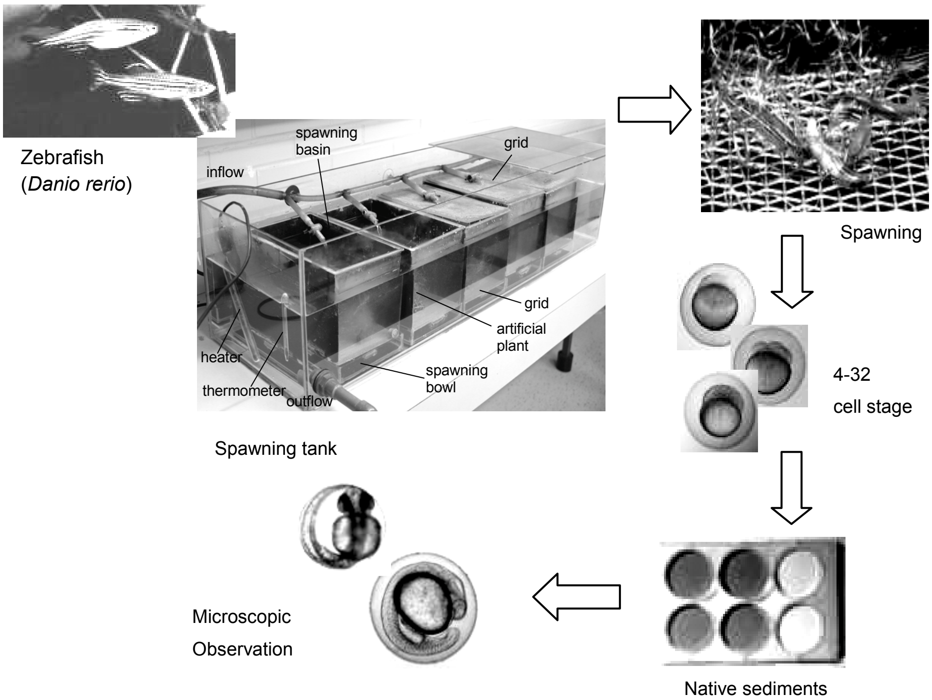

Figure 2: Simplified diagram showing the major steps in the zebrafish embryo contact assay.

6.3 Important finding

The novel contact assay with zebrafish embryo was initially applied for the general assessment of sediments collected from German rivers. Here we will present some important results from these studies (HOLLERT et al. 2003, KEITER et al. 2006):

1. *The zebrafish embryo test detects contamination levels of aquatic sediments.*

To evaluate the embryotoxicity of sediments temporarily resuspended by currents caused by shipping traffic, a fish-spawning site connected to the Neckar River (Eberbach 2) was examined in comparison to a reference site (Eberbach 1) near the outflow to the Neckar River (Figure 3). A very high mortality was observed at Eberbach 2 site. In addition, prolonged exposure increased the mortality of zebrafish embryos significantly. On the other hand, the lack of embryotoxic effects in sediments from the site Eberbach 1 documents that the zebrafish embryo contact assay is capable of identifying non-toxic native sediments comparable to those of W4 quartz powder and pure water controls. In another study, a significant retardation in development was observed among zebrafish embryos after 24, 48 and 72 h incubation with native sediments from Ehingen along the upper Danube river (Figure 4).

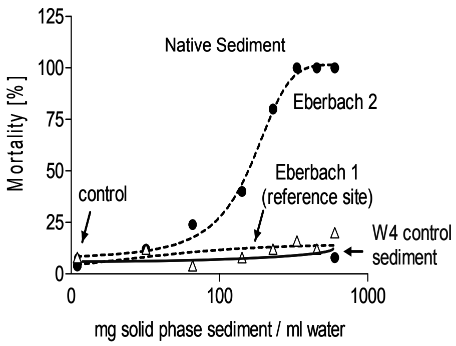

Figure 3: Embryotoxicity of two native (solid phase) sediments from a fish spawning site in a prolonged zebrafish embryo assay with an incubation time of 144 h. 3 g SiO powder (grain size W4) as negative controls. (redrawn from HOLLERT et al. 2003).

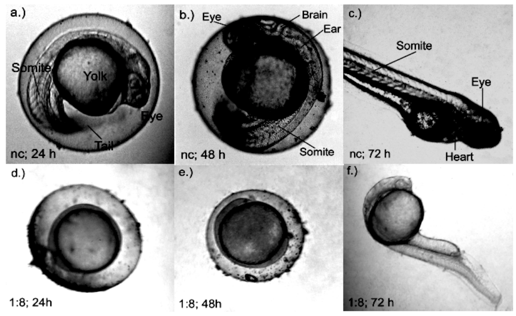

Figure 4: Embryos of zebrafish after (a) 24, (b) 48 and (c) 72 h incubation with standard water (as negative control) and (d) 24 , (e) 48 and (f) 72 h incubation with native sediments from the upper Danube river. Location Ehingen 53.6 mg/ml. (adopted from KEITER et al. 2006).

2. *The zebrafish embryo test reveals that pore water underestimates the bioavailability of lipophilic substances.*

Figure 5 provides a survey of the embryotoxicity of native pore water samples from native sediments, as determined by means of the zebrafish egg assay. The pore water (Forellenbach 1) downstream a sewage treatment plant induced a mortality of 20 %, whereas there was only a small difference to the reference site (Forellenbach 2) with comparable geological background.

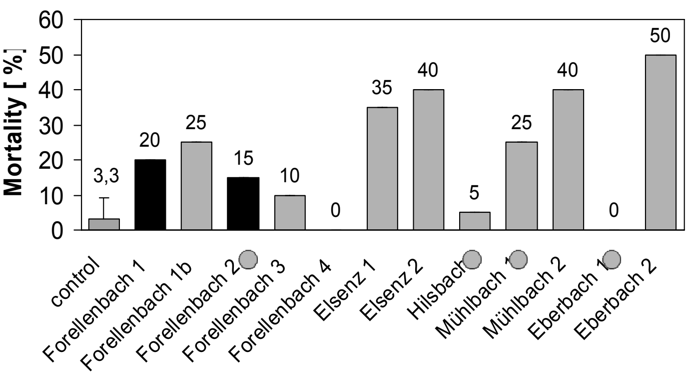

Figure 5: Embryotoxicity of undiluted native pore waters in the fish embryo assay with zebrafish (*Danio rerio*) using 20 fish eggs for each sample after 48 h of incubation. The mortality of the control is given as median and standard deviation from 3 independent experiments (redrawn from HOLLERT et al. 2003). Reference sites with dots.

3. *The zebrafish embryo test identifies whole native sediment as promising for providing a more comprehensive and realistic insight into the bioavailable hazard potential of sediments whereas acetonic extracts can be used as rough estimate of embryotoxicity*

Figure 6 compares toxicity of (a) native sediment and (b) acetonic extracts of sediments from the Forrellenbach stream. Compared to whole sediment exposure, greater mortality was shown by embryos exposed to organic extracts. However, since whole sediment-exposed embryos also revealed significant developmental defects, this exposure phase served as the more realistic exposure scenario.

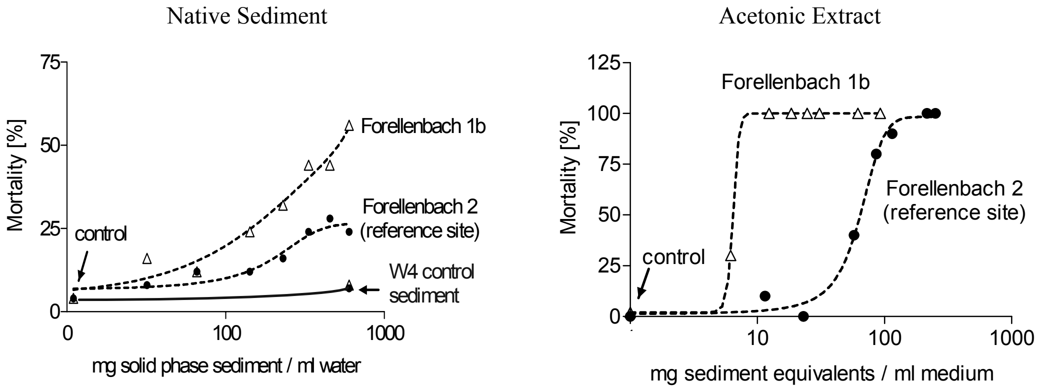

Figure 6: Embryotoxicity of two acetone sediment extracts (right) and whole sediments (left) in the zebrafish (*Danio rerio*) embryo assay after 48 h incubation (Redrawn from HOLLERT et al. 2003)

As mentioned earlier, through the SeKT joint project, the fish egg contact assay with *Danio rerio* has been successfully enhanced and improved as regards to the following:

1. The test system has been optimized to make it more suitable for native sediment samples.
2. As for oxygen, the actual concentration available for the fish egg is more crucial than the overall concentration in the water phase. In addition, gentle shaking can facilitate the distribution of available oxygen and thus, reduce developmental retardation due to hypoxia.
3. Dose-response relations using spiked samples can be determined for heavy metals as well as for organic substances.
4. The fish egg contact assay can distinguish between a broad range of different effect potentials in various sediment types.
5. By applying colloidal silica, the recovery rate of fish eggs can be significantly increased.

6.4 Future prospects

The fish egg contact assay with *Danio rerio*, as detailed above, is indeed a very promising tool for assessing the bioavailable hazard potential of sediments. One major drawback of the said assay, however, is that it can only provide details on the embryotoxic (mortality, teratogenic malformations, hatching delay, etc) potential of contaminated sediments. There is no information on which biochemical mechanisms have played a role and brought about such organismic responses. Through the development of various mechanistic-based bioassays which parallel the sediment contact assay test with zebrafish embryos, it is now possible to integrate them to be able to provide greater insights or evidences into the hazard potential of sediments. In other words, such emerging approach intends to link the observed lethality and morphological aberrations observed in sediment-exposed embryos with what is happening at the biochemical and cellular levels. After exposure of embryos to sediment for a defined period of time (usually 48 h), they can be further analyzed for possible genotoxic, mutagenic, dioxin-like, proteotoxic, immune modulation, and estrogenic responses due to sediment-borne contaminants. In this way, the fish egg contact assay can expand the framework for Weight-of-Evidence (WOE) approach to risk evaluation. For instance, if sediment samples were found to cause embryotoxicity in zebrafish embryos and there was a strong correlation with induction of comets (assay for genotoxicity), these results could intensify the evidence on the presence of harmful substances. Since this idea is relatively novel, only a very few studies have so far utilized a sediment contact test with zebrafish embryos coupled to mechanistic-based bioassay to characterize biological activities of contaminants in aquatic sediments. One study, for example, reported the detection of single-strand breaks in zebrafish embryos by the comet assay to demonstrate the genotoxic effects by exposure to model compounds or river sediments (KOSMEHL et al. 2006). Prior to that, another study revealed weak to strong upregulation of hsp 70 levels (as a measure of proteotoxicity) among zebrafish embryos exposed to both whole- and organic extracts of sediments obtained from a tropical lake (HALLARE et al. 2005). More recently, gene expression analyses using DNA arrays with approx. 20.000 genes have been applied with both sediment extracts and native sediments (KOSMEHL et al. submitted). More challenging attempt could be the use of early-stage zebrafish embryos to investigate aryl hydrocarbon receptor (AhR)-mediated toxicity of sediment samples (e. g. dioxin-like responses, endocrine disruption). Surely, the fish egg sediment contact assay with *Danio rerio,* being a relatively new method in sediment toxicology, will have a long way to go. It is open to challenges for future research.

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Benefit from standardisation, regulatory and scientific requirements, procedures and participations

Hans-Jürgen Pluta

Zusammenfassung

Das Umfeld der Normungsarbeiten, die daran Beteiligten und das Normungverfahren selbst können aus verschiedenen Blickwinkeln beurteilt und bewertet werden. Aus Sicht einer Methodenentwicklung betreibenden Forschung, der Verwaltung oder Rechtssetzung, deren Ziel der vorsorgende Umwelt- und Gesundheitsschutz ist und nicht zuletzt aus Sicht der "Normer", deren Ziel in der konstruktiven Interaktion zwischen allen Beteiligten besteht, werden die Leistungen, Vorteile und Anforderungen an die Normung beschrieben. Das Ziel des im Normungsbereich engagierten Personenkreises besteht in der aktiven Einbindung aller Beteiligten in den gesamten Prozess, der zur Bereitstellung guter, genormter und praxistauglicher Verfahren führen soll, bei denen selbstverständlich bereits seit mehr als 20 Jahren alle erforderlichen Elemente der Qualitätssicherung verankert sind. Verschiedene nationale, internationale und europäische Rechtssetzungen, wie das Wasserhaushaltsgesetz oder die Wasserrahmenrichtlinie beinhalten oder verweisen auf spezielle Regelungen und beziehen sich in speziellen Anhängen auf die verbindlich vorgeschrieben Verwendung von genormten Mess- und Analysenverfahren, wie chemisch-physikalische Messverfahren und Biotests. Wissenschaftliche und regulatorische Anforderungen, formaleVerfahrensabläufe, Beteiligungen und Einbindungen werden grundsätzlich und anhand von Beispielen beschrieben und diskutiert. Ziele und Inhalte der Normungsarbeit, deren Ergebnisse, Verwendung im Bereich der Umweltüberwachung und -politik und die daraus resultierenden Vorteile sollen einen etwas vertieften Einblick geben und vielleicht das Verständnis der Zusammenhänge sowie die Akzeptanz der aktiv Beteiligten am Normungsprozess erhöhen.

Summary

The working field of standardisation and standardisation itself can be evaluated from different point of views. Benefits and requirements are presented from the perspective of a researcher, developing analytical methods, the view of an administrator or regulator trying to protect environmental and/or human health and – last but not least – the view from a "standardiser", who is interested to interact with the different participants and to involve them

into the standardisation process in order to establish sufficient and useful tools considering QA aspects. Different national, international and European regulations as Federal Water Act or Water Framework Directive include, are followed by or connected with specific rules and standards cited in specific annices, referring to standardised methods and procedures like standards for chemical analysis and biotesting. Regulatory and scientific rquirements, procedures, participations and involvements are described and discussed in general and based on examples. Objectives of standardisation work, results, their use in environmental policy and following benefits will give a view and perhaps enhance the understanding for the active participants/institutions in standardisation processes.

1 Introduction

Standardisation is an important and helpful requirement for products, governmental law-making legislation as well as administration and for scientific work.

Regarding standardisation of products, successful, high class companies set and create standards. They use product-, production- and measurement standards as integrated part of their marketing strategy.

Referring to standardisation in governmental law-making legislation and administration, analytical standards are used. Different acts and ordinances, e. g. Water Framework Directive (European), Federal Water Act (national), Wastewater Ordinance (national), Waste Water Charges Act (national) are in every case followed by and connected with rules and standards cited in specific annices and referring to standardised methods and procedures – for example standards for chemical analysis and biotesting.

In the field of scientific work standardisation is an inherent element of good scientific praxis (no one wants to have or publish results from the „series of unreproducible experiments“).

After research work, a method description (methodology) is indispensable prior to publication – this is the first step to „standardisation“. The only question, which has to be answered is, if a formal standardisation is necessary and how it should be done.

This contribution is focussing on and to open the view, the comprehension and perhaps the understanding for the active people and institutions in standardisation work – of course including sediment tests as well as to give an idea on regulatory and scientific requirements, procedures and participations within standardisation procedures. This will be done using as example the chemical and biological methods for water and sediment analysis.

2 What does standardisation want to achieve?

Referring to general concepts, strategies and aims, standardisation wants to achieve

> attendance of all interested parties, independent from economic performance and language skills
> participation on and contribution to international and European standardisation
> national transfer of international standards

- > uniformaty and consistency of a set of standard specifications
- > avoidance of duplication of work
- > consideration of provisions of law

National standardisation institutes contribute actively to get consensus.

3 Example: waste water monitoring

Standardized methods for chemical/physical analysis to monitor the function and efficiency of technical facilities for waste water treatment (e. g. concentration of phosphorus and nitrogen) and for biotests to monitor the possible ecotoxigological effects of treated wastewater are required methods of the national Federal Water Act, Wastewater Ordinance und Waste Waste Charges Act.

Referring to biotests, the following general requirements have to be fulfilled:

- > **Operational** (Test result gives a direct and evident indication about objective and quality of a waste water treatment procedure.)
- > **Reproducibility** (standardised method)
- > **Lawful** (Determinations and definitions referring to a test and sampling procedure lead to results which can be used within legal proceedings.)
- > **Legal security** (intrinsic quality assurance, data about measurement uncertainty)
- > **Evidence** (representative status of used organisms or clear recording of an effect)
- > **Compatibility with EU-Regulations** (total nitrogen)
- > **Compatibility of national regulations, Waste Water Ordinance and Waste Water Charges Act** (salinity-caused toxicity)

A set of biotests is in use or has been proposed in different regulations. The biotests have been standardised at national (DIN/DEV), European (CEN) and international level (ISO). By choosing different organisms, this set covers at moment aspects of representativity, trophic levels, level of organisation and ecotoxicoloical effect level (figure 1). It is not completed and supplementary biotests for e. g. the detection of genotoxic, endocrine and immunotoxic effects are under development and/or within the standardisation process.

Formal procedures lead from a working draft to a national standard, an ISO standard or a CEN standard (vertical in figure 2). Between these three standardisation procedures there are – from time to time a little bit complicated – possibilities of interconnection at different development stages (horizontal in fig.3). However, finally a national standard (e.g. DIN), an European standard (EN), an international standard (ISO) or combinations (DIN EN, DIN EN ISO, EN ISO) will be received. European countries are forced to use European/international standards within their regulations and to replace the corresponding national standard.

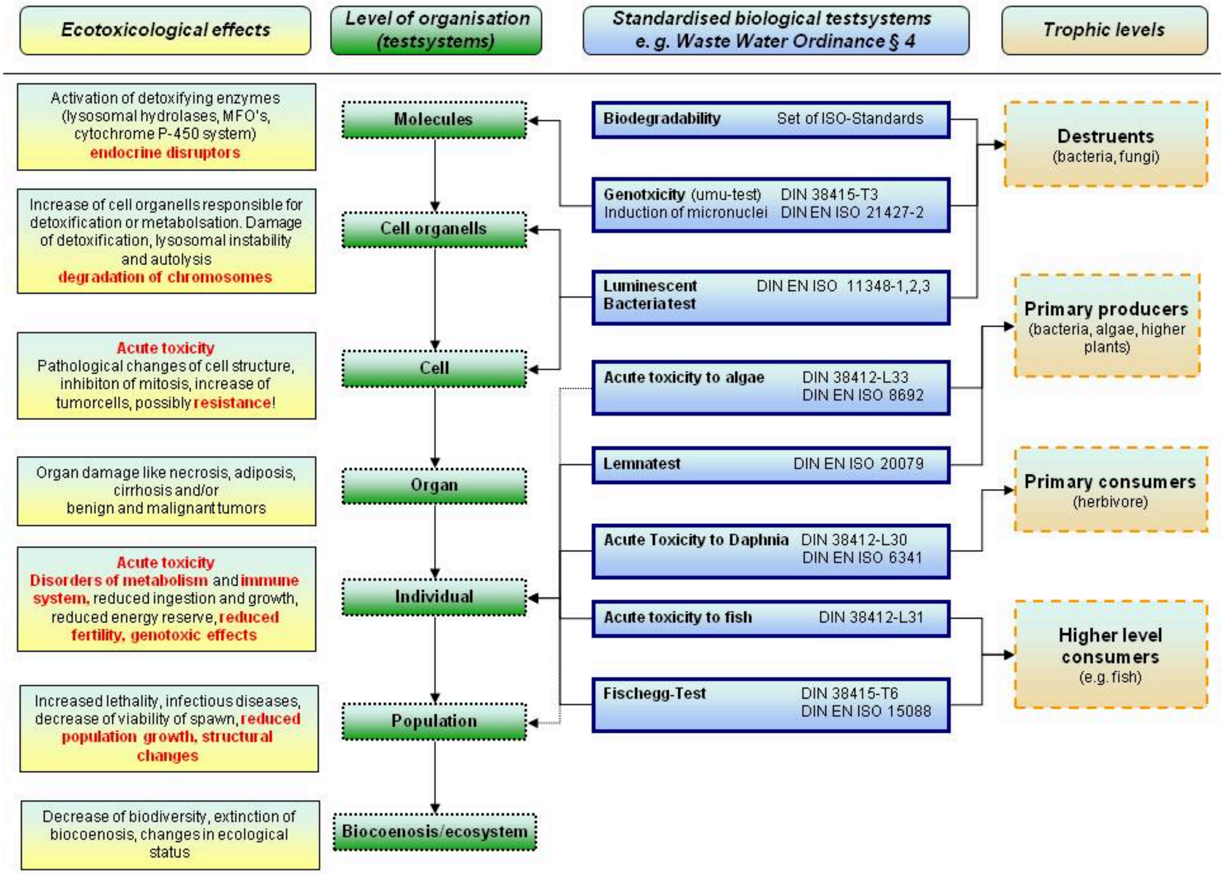

Figure 1: Representativity, trophic levels, level of organisation and ecotoxicological effect levels covered by sets of biological ecotoxicity tests

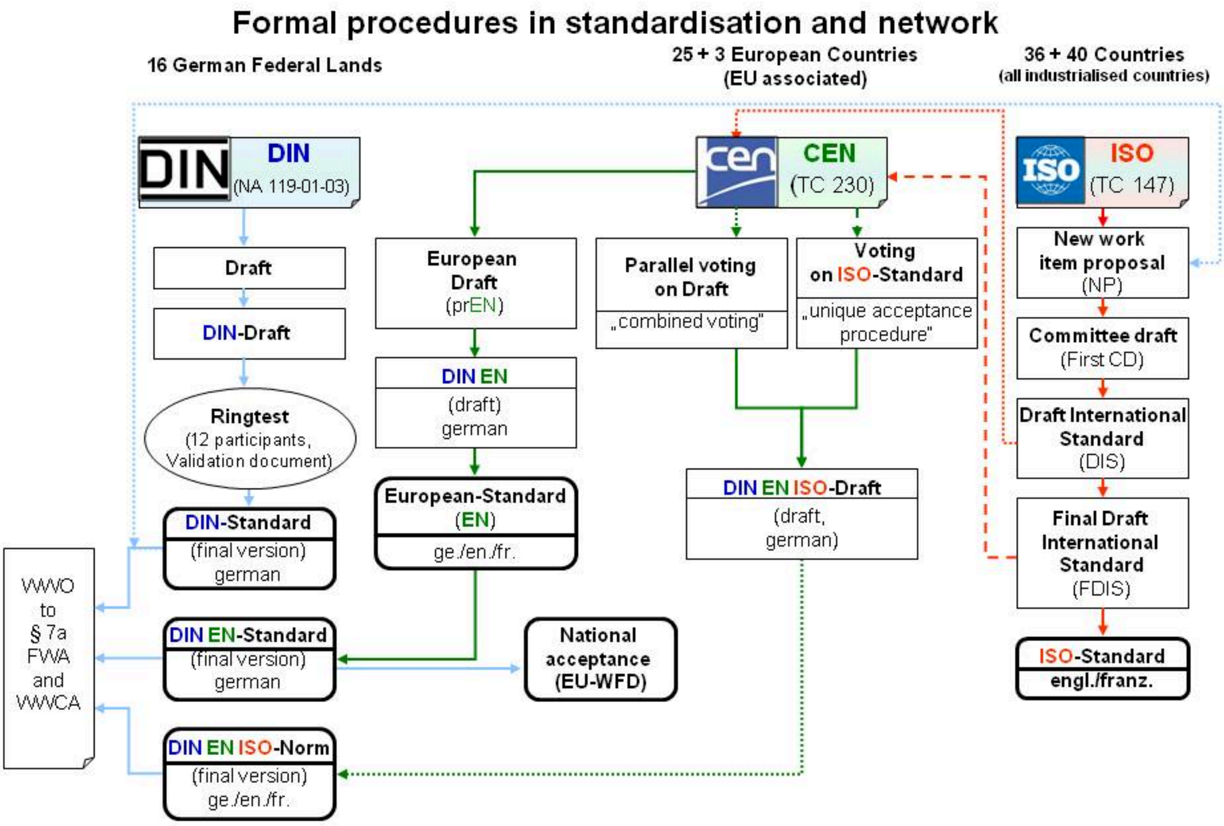

Figure 2: Formal procedures in standardisation and network

4 Contributions, co-operation, scientific community

At national level different working groups are involved developing analytical methods. Generally they are composed by representatives from administration, industry, universities, private laboratories, research institutes and equipment manufacturers. With their experimental work in laboratories, practical developments, and scientific basic studies they are responsible for the input to the respective working groups at scientific level. The advantage of this working group composition takes into account aspects of scientific research, performance of measurement in practise an development in equipment. The discussions and enacted work programme leads to a scientific network, which is described in figure 3 at national as well as at international level.

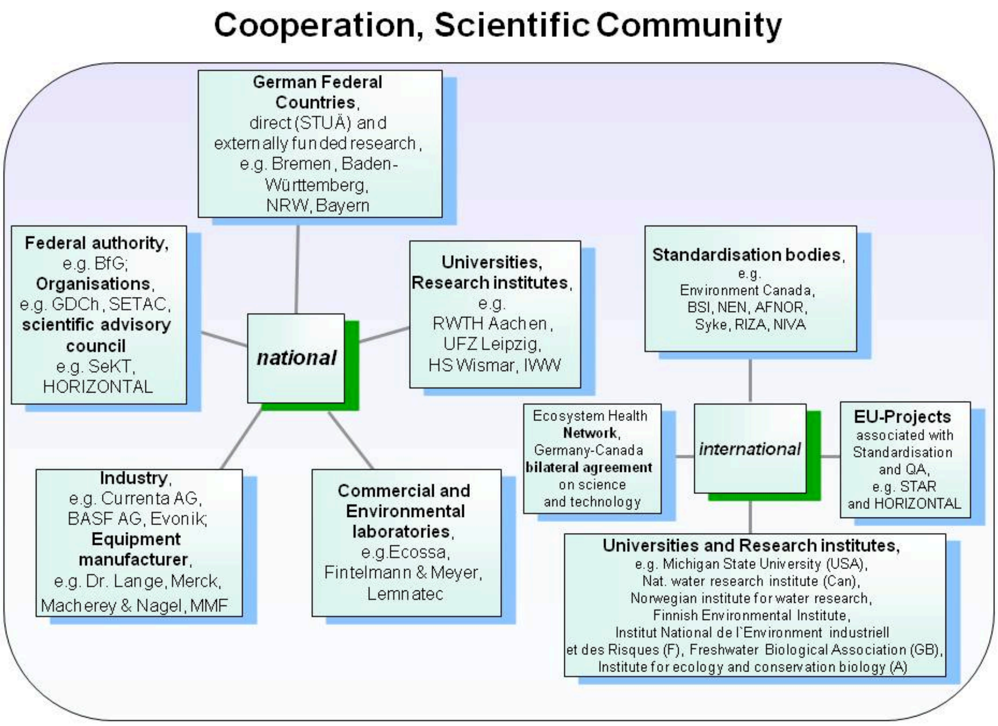

Figure 3: Cooperation, scientific network at national and at international level

5 Formal aspects of standardisation

The formal structure of ISO TC 147 is shown in figure 4.

The development of a standard requires certain, defined steps and participates all member states:

> At Working Group (WG) level: **Proposal** of WG-members, nominated experts or national standardisation body, regulary **based on a working document**.

> Decision of the respective WG, to ask for **New Work Item Proposal (NWIP)**, noted in a resolution.

> Decision upon the **responsibility** for the proposed standard. The **convenor** can give it to a **project** leader – based on the decision of the WG and also noted in a resolution.

> **Report** of the WG-convenor to next formal level, which is a **Subcommittee (SC)**.

> If **SC** accepts the recommendation of a WG for a NWIP, it has to be noted in a resolution addressed **to TC-level** (At SC-level, a nominated secretary is responsible for all formal actions including all WGs covered by the respective SC.).

> **Report** of the SC-convenor **to TC-secretary** (regulary during a plenary meeting). Usually the TC accepts the recommendation of WG/SC and put it into a resolution.

> Based on this resolution, the secretary of a **TC is** allowed and **responsible to ask for a formal vote** (Central secretary, CS).

> The formal vote is launched, and a WD is included. If the voting is successful, a **NWIP is officially registered at ISO Work Programme**.

> A **time scale** will be set **and comments** to the proposal from formal voting will be given **to respective convenor** at SC-level and to Convenor at WG-level.

> At WG-level, **comments** have to be discussed and answered using official templates. In case of no significant disagreements, a **revised document** will be sent to SC- and TC secretary **for further proceeding** as ISO CD.

> During the whole procedure TC-, SC-secretary and convenors of WGs are responsible for the distribution of all relevant information. This is usually done by TC-secretary using livelink.

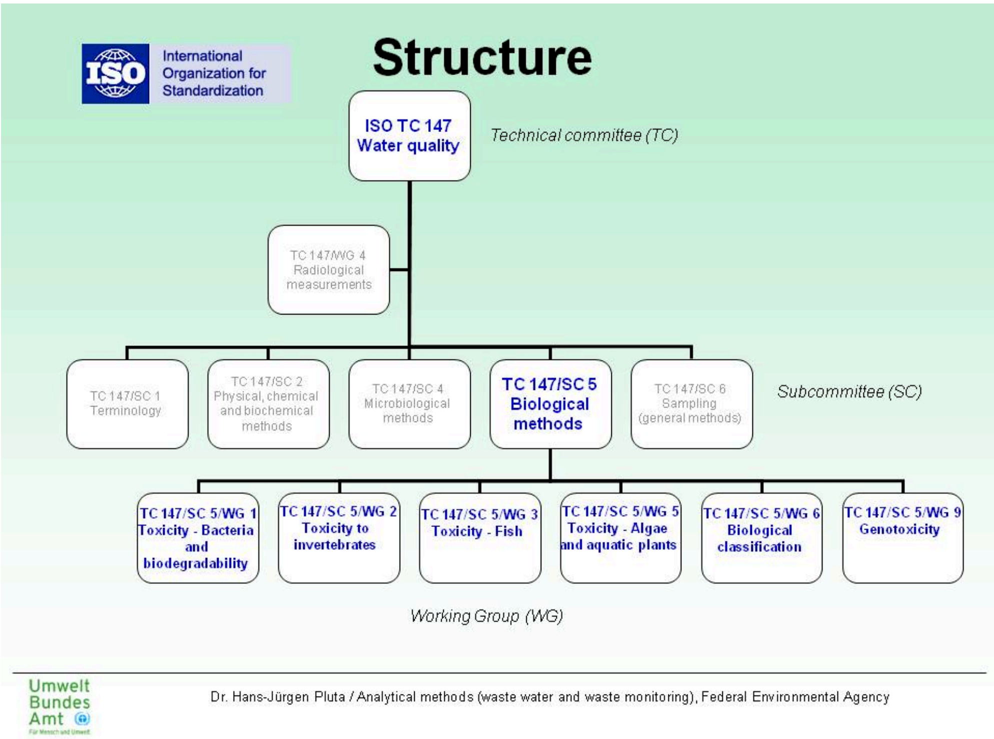

Figure 4: Formal structure of ISO TC 147

Further proceeding depends on the determinated time schedule and follows the scheme, described in figure 5.

> Proceeding to ISO CD and to ISO DIS

> During DIS-stage, a validation of the method is required.

> Proceeding to ISO FDIS (only editorial changes at that stage)

> After acceptance by voting: publication as ISO-Standard

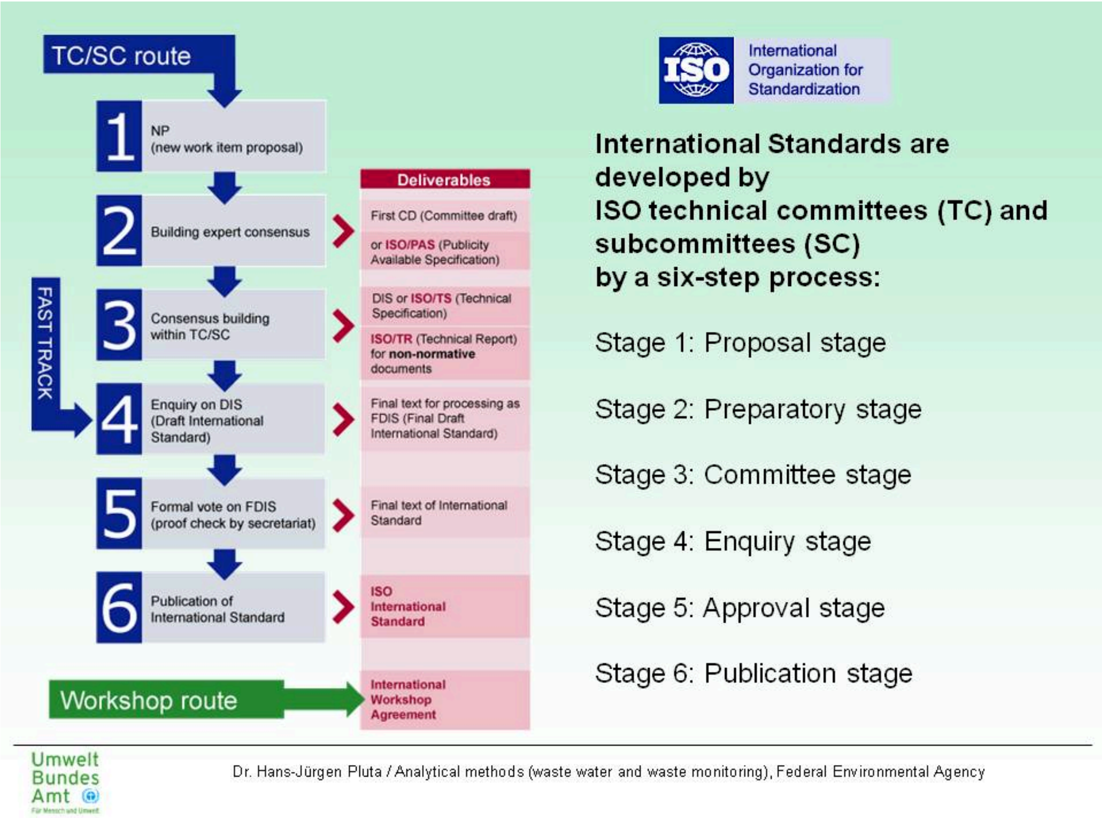

Figure 5: Development of an international standard

There are some specific aspects, which have to taken into account during standardisation procedure:

> WGs propose, if a standard or a Technical Specification (TS) has to be developed

> Possibility, to take into account important specific interests of a member body by creating an informative annex

> If an EN-standard is proposed by a WG, the respective working group in CEN TC 230 has to ask for that by resolution based on the Vienna agreement.

For sediment testing the following standards or standards in preparation are available:

> **DIN EN ISO 20079:** Water quality – determination of the toxic effect of water constituents and waste water on duckweed (*Lemna minor*) – duckweed growth inhibition test

> **DIN EN ISO 15088:** Water quality – determination of acute toxicity of waste water to zebrafish eggs (*Danio rerio*)

- **ISO CD 10871:** Water quality – determination of the inhibition of dehydrogenase activity of *Arthrobacter globiformis* – solid contact test using the redox dye resazurine
- **ISO CD 21338:** Water quality – kinetic determination of the inhibitory effects of sediment, other solids and coloured samples on the light emission of *Vibrio fisheri* (Kinetic luminescent bacteria test)
- **ISO CD 10872:** Water quality – determination of the toxic effect of sediment and soil samples on growth, fertility and reproduction of *Caenorhabditis elegans* (Nematoda)
- **Possible NWIP:** Sediment contact test with *Myriophyllum aquaticum*

6 Benefit from standardisation

The benefit from standardisation is summarised as follows:

- standardised and accepted „fit for purpose"-methods
- comparable and lawful results within Europe and worldwide – most important for regulators and administrators
- comparable assessment of environmental impact and quality status of freshwaters, transitional waters and sediments
- standardised and validated methods as tools for quality assurance and formal accreditation
- ISO – network for use as platform (scientific discussions, further needs, developments, pre- and co-normative research, mandated projects)

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Standardization according to OECD rules: Sediment toxicity test with *Lumbriculus variegatus*

Philipp Egeler and Thomas Knacker

Zusammenfassung

Im regulatorischen Bereich begann die Chemikalienprüfung mit dem *Lumbriculus variegatus*-Toxizitätstest 1999. Im Jahr 2003 wurde ein erster Entwurf einer Testvorschrift erarbeitet und ein Ringtest vorbereitet. Der Ringtest wurde 2004 abgeschlossen und ausgewertet. 2005 erschien der Bericht zur Methodenvalidierung einschließlich eines überarbeiteten Testvorschriftsentwurfs. 2007, nach erfolgter Kommentierung des Entwurfs, einer erneuten Überarbeitung und seiner Bestätigung durch die nationalen Koordinatoren, wurde die Testvorschrift von der OECD als Testvorschrift Nr. 225 angenommen.

1 Introduction

The OECD Chemicals Testing Programme was launched in 1977. It produced a series of OECD Test Guidelines grouped into four different sections: physical-chemical properties, effects on biotic systems other than man, degradation/accumulation, and health effects. In 1981, the OECD Updating Programme for Test Guidelines was established which, in 1990, was renamed OECD Test Guideline Programme (TGP). The task of the TGP is, *inter alia*, to promote the development of methods for obtaining needed test data, to initiate and undertake the development of practical test guidelines and to periodically review the Test Guidelines and revise them as needed. These activities of the TGP are related to OECD's principles for testing and assessment of chemicals, i. e.,

(1) to assess the potential effects on human health and environment of chemicals prior to marketing;
(2) to make testing of chemicals more systematic and cost effective within an international framework.

The Guidance Document for the Development of OECD Guidelines for the Testing of Chemicals (OECD 2006) describes the structure of the TGP, the various responsibilities of those involved in the process and the procedures when developing new or updating existing Test Guidelines. The OECD Secretariat, individual member countries of the OECD or the scientific community can take initiative for proposing a new or updating an existing testing method based on valid arguments as, for example, regulatory needs, scientific progress in hazard assessment, international harmonisation, animal welfare, reduced costs without loss of essential information. The Working Group of National Co-ordinators of the TGP (WNT) sets the priorities of the proposed guideline development activities and identifies the lead country for each activity.

Keeping in mind the briefly outlined rules of the OECD to develop new Test Guidelines we will describe in the following some important steps which led to the adoption of the OECD Guideline No. 225 "Sediment-Water *Lumbriculus* Toxicity Test Using Spiked Sediment" (OECD 2007).

2 Development of the guideline with *Lumbriculus*

2.1 Rationale for the test

The Technical Guidance Document for EU-Risk Assessment for New and Existing Chemicals (EC 2003) and, more recently, the Guidance for the Implementation of REACH (ECHA 2008) describe the strategy for biological testing of sediment dwelling organisms with substances that show log K_{OC} or log K_{OW} values ≥ 3. To adequately address the various routes of exposure for benthic organisms a test battery with the epibenthic larvae of the non-biting midge *Chironomus riparius* or *C. tentans*, the endobenthic oligochaete worm *Lumbriculus variegatus*, and a third species, e. g. the epibenthic amphipod *Hyalella azteca*, is recommended (EC 2003, RIEDHAMMER & SCHWARZ-SCHULZ 2001). Despite the regulatory need for a battery of sediment dwelling organisms, a standardised testing method for endobenthic organisms was not available when tests were requested by authorities at the beginning of this century. Based on data presented by PHIPPS et al. (1993), US EPA (2000), and BRUST et al. (2002), and along with experiences generated when testing the toxicity of aromatic amines to benthic organisms, a proposal for an OECD guideline on testing the toxicity to the sediment dweller *L. variegatus* was developed. An overview of the test design is shown in Table 1. The German National Co-ordinator of the TGP submitted the proposal to the OECD; and the WNT prioritised the activity, identified Germany as the lead country and required the validation of the proposed testing method.

2.2 Validation and acceptance of the test

In 2003 and 2004 an inter-laboratory comparison test was commissioned by the German Federal Environmental Agency (UBA; R&D-Contract-No. 202 67 429) to ECT Oekotoxikologie GmbH. Fourteen laboratories from seven different countries (Belgium, Germany, Finland, Italy, Switzerland, UK, USA) participated and determined the EC_{50} and NOEC/LOEC values of the model compound pentachlorophenol on reproduction (total number of individuals), biomass (dry weight) and mortality (dead and missing worms) of *L. variegatus* (see Table 2).

The validation of the testing method was considered as being successful. The endpoints reproduction (total number of worms at the end of the test) and growth (total dry biomass at the end of the test) were accepted as suitable, whereas the endpoint mortality was thought as being not suitable since mortality is masked by the reproduction of the worms. Hence a Draft Guideline was prepared by ECT Oekotoxikologie GmbH; the Draft Guideline was submitted by the German National Co-ordinator of the TGP to the OECD Secretariat. The Secretariat initiated two consultation rounds and received comments on technical issues, on the relevance of biological parameters and endpoints, and on statistical evaluation from Danish, Finnish, German, Dutch, Swedish, British and US national experts. Comments were also received from the Business and Industry Advisory Committee to the OECD (BIAC).

Table 1
Sediment toxicity test with *L. variegatus* - Summary of Test Design

Parameter	
Test organism	*Lumbriculus variegatus* (Müller), synchronised adult worms of similar size
Test sediment	spiked artificial sediment; peat content 5% of sediment d.w.; addition of *Urtica*- and cellulose-powder (0.4 - 0.5% on dry sediment) before application of test item; no additional feeding
Overlying water	reconstituted water according to OECD guideline No. 203 (OECD 1992); sediment water ratio approx. 1 : 4
Control media	uncontaminated artificial sediment and reconstituted water (sediment water ratio approx. 1 : 4)
Endpoints	Reproduction and survival, biomass (dry weight) (EC_x and/or NOEC/LOEC)
Test duration	28 d
Temperature	20 ± 2°C
Test chambers	e.g., 250 to 300 mL glass beakers, with lid
Feeding during exposure	no additional feeding during exposure
Water renewal	static; periodic addition of evaporated water
Sediment conditioning	1 week
Number of organisms per test chamber	10 at start
Validity of test	pH between 6 and 9; oxygen above 30% of ASV; reproduction in control replicates: increase of total number of worms by a factor of ≥ 1.8

Table 2
Results of the inter-laboratory comparison test on determining the toxicity of pentachlorophenol to the reproduction, biomass and mortality of *L. variegatus*

interlaboratory comparison	**reproduction**			**biomass**			**mortality**		
	EC_{50}	**NOEC**	**LOEC**	**EC_{50}**	**NOEC**	**LOEC**	**LC_{50}**	**NOEC**	**LOEC**
	(mg/kg sediment d.w.)			**(mg/kg sediment d.w.)**			**(mg/kg sediment d.w.)**		
interlab mean	**23.0**	**9.9**	**27.9**	**20.4**	**9.3**	**25.7**	**25.3**	**16.5**	**39.1**
min	**4.0**	**2.1**	**4.7**	**7.3**	**2.1**	**2.1**	**6.5**	**2.1**	**4.7**
max	**37.9**	**22.7**	**66.7**	**39.9**	**20.0**	**50.0**	**37.2**	**40.0**	**66.7**
interlab factor	**9.4**	10.7	14.2	**5.5**	9.4	23.5	**5.7**	18.8	14.2
SD	**10.7**	7.2	19.4	**9.1**	6.6	16.8	**9.4**	10.3	18.1
CV (%)	**46.3**	72.3	69.4	**44.5**	70.4	65.5	**37.4**	62.4	46.2
geometr. mean	**19.9**	7.6	20.9	**18.2**	7.4	19.4	**23.1**	12.8	32.6

Abbreviations: EC_{50} effect concentration, affecting 50% of the organisms; NOEC no observed effect concentration; LOEC lowest observed effect concentration, SD standard deviation, CV coefficient of variance, d.w. dry weight

After addressing the comments, the WNT approved the Test Guideline which was then reviewed and endorsed by the Joint Meeting of the Chemicals Committee and Working Party on Chemicals, Pesticides and Biotechnology and the Environment Policy Committee (EPOC). EPOC submitted the proposed Guideline to the Council which formally adopted the Test Guideline on October 16, 2007.

2.3 Modification of the test for use with natural sediments

The test method was applied also for assessing contaminated field sediments. However, since the *Lumbriculus* toxicity test was developed for investigating the impact of individual chemicals, the method as described in OECD guideline 225 (OECD 2007) received several technical modifications before use in field sediment testing. The following table shows the major modifications which were done in the frame of a BMBF-sponsored joint research project, "Definition von Referenzbedingungen, Kontrollsedimenten und Toxizitätsschwellenwerten für limnische Sedimentkontakttests (SeKT)".

Modified item	OECD Guideline 225	SeKT (Sedimentkontakttests)	Modified item
Conditioning of sediment-water system	7 days prior to spiking	one day conditioning of field sediments	Conditioning of sediment-water system
Feeding mode	feed in sediment prior to spiking; (max. exposure)	periodical feeding with uncontaminated fish food during exposure	Feeding mode
Assessment parameter: Biomass	total worm dry weight	ash-free dry weight to account for varying ash contents of field sediments	Assessment parameter: Biomass

Summary

Regulatory testing of chemicals with the *Lumbriculus variegatus* toxicity test was started in 1999. In 2003, the first draft test guideline was prepared, and a ring test was initiated. By 2004, ring testing was finished and evaluated. In 2005, the method validation report was issued including a revised guideline proposal. By 2007, the draft guideline was commented, revised again, approved by the National Co-ordinators, and adopted by the OECD as test guideline No. 225.

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Standardization according to the ISO rules. Case: Kinetic luminescent bacteria test for sediment samples

Juha Lappalainen

Zusammenfassung

Toxizitätsteste mit dem Leuchtbakterium *Vibrio fischeri* sind im Vergleich mit anderen Ökotoxizitätstestvefahren sehr schnell. Ihre Korrelation zu Testsystemen mit höheren Organismen ist erwiesen und die Methodik wurde für Wasserproben standardisiert (ISO 11348). Leider ist es schwierig, die ISO-Standardmethode bei Feststoff- und Sedimentproben anzuwenden. Zur Überwindung der methodischen Schwierigkeiten, die bei Sedimentkontakttesten mit Leuchtbakterien auftreten, wurden verschiedene Lösungen gefunden. Da die Zusammensetzung der Probe eine wesentliche Rolle spielt, ist der direkte Kontakt der Bakterien mit dem Probenmaterial ausschlaggebend. Verluste an Indikatororganismen durch Anlagerung an Sedimentpartikel können genauso wie optische Störungen durch Schweb- oder Farbstoffe bei einigen der vorgeschlagenen Testsysteme zu falschen Einschätzungen der Toxizität führen.

Gegenwärtig befindet sich der hier vorgestellte kinetische Leuchtbakterientest im Standardisierungsverfahren. Bei dieser Methode erfolgt die Korrektur von Farb- und Trübungseinflüssen durch kinetische Messung. Diese Methode ist bei unterschiedlichen Luminometern anwendbar, die mit einem Dispenser ausgestattet sind, vorausgesetzt, dass sie gleichzeitig messen und verteilen können. Zudem ermöglicht diese Methode den Einsatz von Leuchtbakterien unterschiedlicher Beschaffenheit (gefriergetrocknet, frisch gesogen, etc.).

Abstract

Toxicity testing with photobacterium *Vibrio fischeri* is very rapid compared to other ecotoxicity tests. The correlation to higher organisms has been proven and the method has been standardized for water samples. Unfortunately, it is difficult to apply the standard ISO method for solid and sediment samples. The methodological difficulties associated with the direct contact test of sediment samples with the luminescent bacteria have resulted in different solutions to overcome the problem. Because the composition of the sample plays an essential role it is very important that the bacteria are in direct contact with the sample. Therefore, the loss of sensor bacteria due to adhesion to sediment particles or optical interference due to particles or colour may result in wrong estimation about the toxicity with some of the proposed systems.

Kinetic luminescent bacteria test is now under standardization. In this method the correction for the colour and turbidity is performed using the kinetic measurement. This method can be used with different luminometers equipped with a dispenser, providing they can measure and dispense simultaneously. In addition, the method allows the use of different bacterial preparations.

1 Introduction

Determination of the inhibitory effects of solid and coloured samples on the light emission of *Vibrio fischeri* has been very complicated or difficult to interpret with the existing standard method for luminescent bacteria (ISO 11348). The difficulty with the photobacteria method for solid and sediment samples questions the relevance of this method. The main reason to use the *V. fischeri* test with samples, where the sample matrix may cause problems, is the speed of the test. With the most used methods there are two main sources of error: loss of sensor bacteria due to adhesion to suspended sediment particles and optical interference of suspended sediment particles.

In order to overcome the current limitations of the assay a novel method was developed and published (LAPPALAINEN et al. 1999). After the positive feed back from the users of the method the standardization process started. There already exists a standard with an annex for the colour correction, however this is complicated because the instrumentation used is different, and a totally new standard was needed. The method utilizing kinetic measurement instead of a single end point measurement was modified from the original publications and validated with different luminometers.

2 Measuring principles

2.1 Kinetic determination of the inhibitory effects of a sample

In the kinetic method the inhibition of light emission by cultures of *V. fischeri* is measured kinetically by following the light emission of cultures from the very beginning of the assay. The photobacteria reagent is dispensed on top of the sample. The change in the luminescence signal is recorded at several readings per second. The maximum signal, which is recorded immediately after all the bacteria are in contact with the sample, is called the peak value. After a contact time of 15 or 30 minutes the signal is recorded again after mixing the sample (Figure 1).

The test criterion is the decrease of the luminescence at each end point compared to the peak value. The correction factor is measured from intensity changes of control samples.

The measurement must be performed as described above because the luminescence can decrease very rapidly with toxic samples and therefore it is of great importance to use a luminometer that can dispense and measure simultaneously (Figure 2).

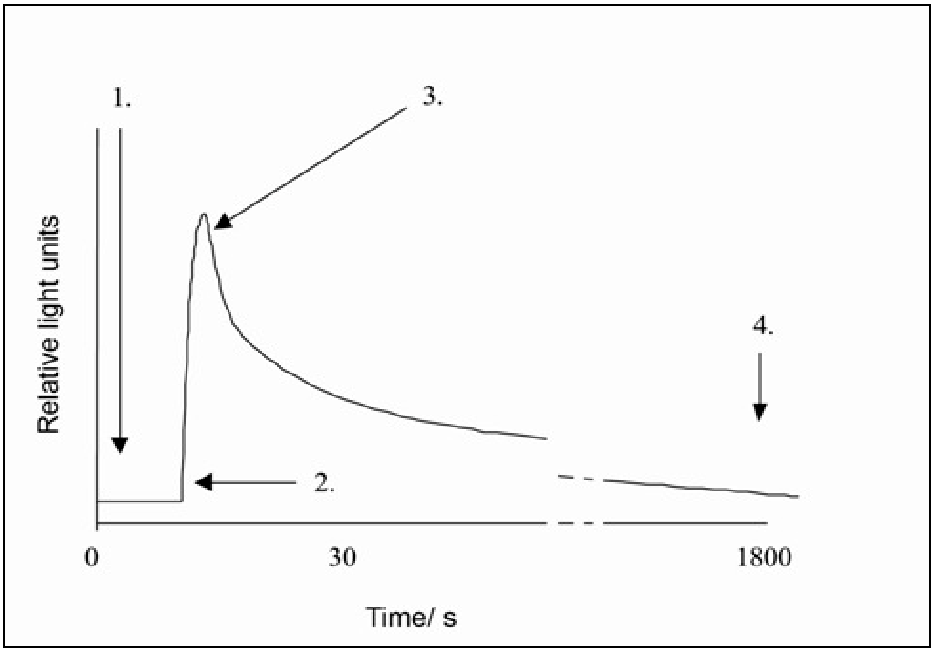

Figure 1: Principal schematic protocol for the kinetic luminescent bacteria test.

Key

1 start measurement	3 record peak value from 0 s to 5 s
2 inject bacteria	4 mix the sample before recording signal at 30 min

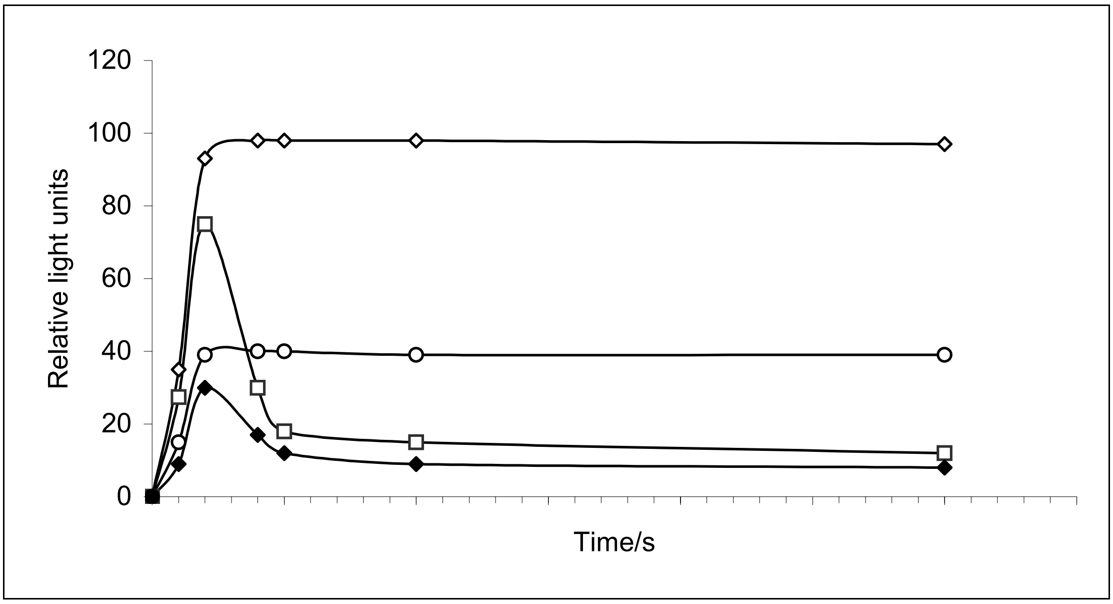

Figure 2: Example of the kinetic determination with different samples.

Key

◊ Response from control (2 % NaCl solution)

□ Response colourless toxicant DCP

◆ Response from a soil sample contaminated with oil

O Response from similar non-toxic soil

2.2 Instrumentation and measuring protocol

In the first publication of the method a Luminometer 1251 from Bio-Orbit, Finland was used. This luminometer is no longer available and it was not possible to apply the instrument protocol that was used for other instruments. Additionally, if the measurement protocol is fixed and only one system is available it is difficult to standardize the method. Therefore, the assay protocol was modified. In this assay design the calculation parameters are fixed but the actual protocol used is slightly different for different instruments e. g. the reagent volumes, timing and temperature. The temperature control inside the instruments to 15 °C is not always available but by incubating the reagent and sample vials in a thermo block outside the luminometer it is possible to keep the temperature close to this during the whole procedure.

It is very important that in every series there is a non toxic control sample for correcting the decrease of luminescence over time independently of the effects of the unknown samples. The measurement conditions, incubation time and temperature, dispensing volumes etc. for this control are the same as for all the samples. Additionally, it is suggested, that in each sample series there is a reference substance included. Therefore the results from the unknown samples are reliable if the measured values for the control and reference meet the test criteria.

The solid and sediment samples are prepared for the assay by weighing the sample and diluting it with the sample diluent, 2 % NaCl solution. Plant roots and coarse particles, larger than 2 mm, must be removed to obtain homogenous suspension.

3 Examples

To fully understand the measurement principle and understand the benefits of the method a simplified example of the measurement is presented here. The samples used were river sediments with an initial concentration of 50 g/l. The samples were homogenised and freeze dried resulting in a fine powder with a strong, brown colour. The results presented here are from the original data but no replicates are shown.

In the ISO standard 11348, measurements the luminescence values of the control sample are compared to the sample luminescence results. Simplified, the luminescence of the unstressed bacteria is compared to the luminescence values of the samples after the contact time. In this example the luminescence value for the control sample after the contact time of 30 minutes is 815 RLUs. For the sample dilutions the luminescence signal is lower but we do not know if the reason is the colour, turbidity or toxicity or any combination of these factors (Table 1). With sample 1, 50 % decrease of luminescence is observed with concentration approximately 12,5 g-1 and with sample 2 approximately 1 g-1.

If the peak values, the luminescence values immediately after all the bacteria are in contact with the sample, are added to the table we notice that with the sample number 1 there is actually no decrease in the luminescence during the 30 min contact time. Therefore, there is no toxicity in this sample to be measured with this method and these sample dilutions.

With the sample number 2 there is a clear dose response effect. With dilutions, which have almost similar peak height as the control sample, the decrease in luminescence is notable. An estimation for the EC50 values can be calculated using these measured values.

Table 1
Measurement data from two different samples. Luminescence signals from the sample dilutions after the contact time of 30 min. Original sample concentration 50 g-1.

Sample 1			Sample 2	
Sample con-centration g –l	Peak height RLU	30 min RLU	Peak height RLU	30 min RLU
0		**815**		**815**
25		184		5
12,5		417		9
6,3		641		35
3,1		807		171
1,6		870		338
0,8		871		480
0,4		854		575

Table 2
Measurement data from two different samples. Luminescence signals immediately after bacterial suspension is added to the sample (peak height) and luminescence signal after 30 min contact time. Original sample concentration 50 g-1.

Sample 1			Sample 2	
Sample con-centration g –l	Peak height RLU	30 min RLU	Peak height RLU	30 min RLU
0	**892**	**815**	**892**	**815**
25	238	184	164	5
12,5	412	417	267	9
6,3	590	641	426	35
3,1	718	807	597	171
1,6	813	870	726	338
0,8	856	871	817	480
0,4	875	854	874	575

4 Summary

The determination of the toxicity with the photobacterium is possible with sediment and soil samples. The correction for the colour and turbidity is performed using the kinetic measurement. This method can be used with different luminometers equipped with a dispenser, providing they can measure and dispense simultaneously. In addition, the method allows the use of different bacterial preparations.

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River basin management: Focus on *in-situ* sediment remediation

Ulrich Förstner

Kurzfassung

Die Sedimentbewirtschaftung unter der Europäischen Wasserrahmenrichtlinie erfordert einen breiteren Ansatz, bei dem *in situ* Technologien in ein modernes System der Risikobewertung und -kommunikation im Flussgebietsmaßstab eingebettet sind. Eine Initiative für europaweite Aktivitäten auf dem Gebiet der Sedimentbewirtschaftung und -technologien könnte im Zuge der kommenden Strategien gegen chemische Verschmutzungen in Oberflächengewässern (WRRL Artikel 16) starten, d. h. zusammen mit dem Maßnahmenprogramm bis 2009 gegen die Quellen von „Prioritären Stoffen“ einschließlich der spezifischen Quellen/Ausbreitungspfade „Historische Verschmutzungen aus Sedimenten“. Angesichts der Größe der Probleme in Europa können weder die theoretischen Handlungsanweisungen noch die praktischen Erfahrungen mit erfolgreichen Problemlösungen in den USA ignoriert werden. Die vorliegende Übersicht zur Einführung in den “SedimentKontaktTest” behandelt vier Themen:

(1) *Konzepte und Optionen für lokale und flussgebietsübergreifende Bewirtschaftungspläne:* standortspezifische und Flussgebietsmodelle, Risiko-Indikatoren, Managementoptionen, Sedimentbewirtschaftung und -monitoring auf verschiedenen Raum- und Zeitskalen

(2) *Hydrodynamik als ein Schlüsselfaktor für kontaminierte Sedimente in Flussgebieten:* BMBF-Schwerpunkt „Sedimentdynamik und Schadstoffmobilität in Fließgewässern“, USEPA-Großprojekte mit chemischen, biologischen und physikalischen Parameterlisten

(3) *Sedimente und WRRL „Vom Monitoring zu Maßnahmen“ mit Beispielen von der Elbe:* Formen des Sediment-Monitoring, pragmatische Ansätze für kontaminierte Sedimente in Flusseinzugsgebieten, Umgang mit Unsicherheiten, Qualitätsstandards, „Traceability“

(4) *Vergleichende Risikobewertung für „Capping“ und „Monitored Natural Recovery“:* Entwicklung in den USA: ökologische Probleme mit traditionellen Ausbaggerungen; Europa: Vorrang von *ex situ* Maßnahmen; künftiger „Markt“ für *in situ* Lösungen?

1 Introduction

Sediment management under the EU Water Framework Directive will need a wider scope with *in-situ* technologies embedded in a modern system of risk assessment and communication on the river basin scale. A new initiative for Europe-wide activities in the field of sediment management technology could start in the course of the forthcoming strategies against chemical pollution of surface waters (WFD article 16), i. e. establishment of a programme of measures until 2009 for sources of priority substances including the specific source/pathway "historical pollution from sediment". In the view of the size of the problems in Europe, the guidance to innovative remedial measures and the experience from successful problem solutions in the United States cannot be ignored. In the present overview around the practical applicability of "SedimentKontaktTests", four major themes will be treated: (i) concepts and options for site-specific and river basin-wide management, (ii) hydraulics – key factor for contaminated sediments in river basins, (iii) "from monitoring to measures" including a section "basin-wide *in-situ* remedial options: examples from the Elbe River".

2 Concepts for site-specific and river-basin wide management

2.1 Sediment assessment and management in river basins: Definitions

Sediment assessment is the characterization of sediment for a given purpose (e. g., evaluations for risks to environmental health, habitat construction, etc.). *Sediment management* is making decisions and taking actions on sediments; it seeks balance between minimizing contaminant risk in the environment and human health and (b) minimizing cost (APITZ & POWER 2002).

A basin-scale assessment involves the balancing of a *Conceptual Basin Model* (CBM, which considers the mass flows of particles and contaminants, screening level assessment of sediment quality and archived data), and basin-scale objectives (BOs) to generate a Basin Use Plan (BUP) (APITZ & WHITE 2003). The *Conceptual Site Model* (CSM) is a three-dimensional description of a site representing the knowledge on the contaminant source area(s), as well as, the physical, chemical, and biological processes that affect contaminant transport from the source(s) through site environmental media to potential receptors (HEISE 2007).

2.2 Site-specific and river basin-wide risk indicators

The aim of sediment management is risk reduction; this includes socio-economic and environmental risks. Risk assessment is an integral part of risk management (ELLEN et al. 2007). *Risk indicators* are a necessary tool to connect risks with management options for sites and river basin (Table 1). They can help simplify complex information, can be used for site prioritization or site-specific raking and can thus trigger management actions (JOZIASSE et al. 2007).

Table 1
Risk indicators and management options for sites and river basins (Joziasse et al. 2007)

Indicators of risk		Management options	
Site-specific	**River Basin**	**Site-specific**	**River Basin**
• High contaminant load • Ecotoxicological effects • Alteration of benthic community • Eutrophication • High number of E. coli or pathogens	• Indicators for habitat losses • High contamination of waters and sediments • Poor chemical and physico-chemical quality • Reduction in migrating species	*In-situ* treatment Capping Function change Turn to river basin management (source control) Sediment basins, dredging, excavations	Negotiations with upstream/down-stream stakeholder Make use of established river commissions (ICPR..) Revisions of industrial or agricultural policies; enforcement of regulations

2.3 Sediment management and monitoring at different scales

Figure 1 presents the process diagram for basin-scale and site-specific sediment risk management. The monitoring at the initial stages is to inform prioritization and decisions, and during the latter stages of the process to assess the outcome of the action and the associated feedback mechanisms for further assessment and action if required (after APITZ et al. 2007).

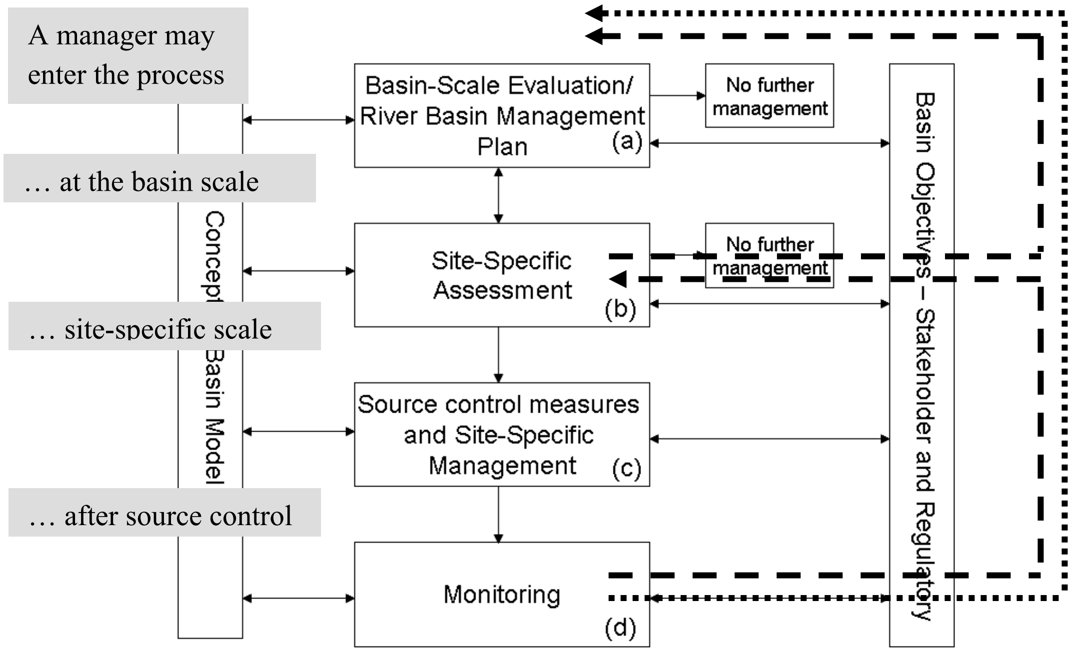

Figure 1: Process diagram for basin-scale and site-specific sediment risk management

It is convenient to consider the quantity aspects, i. e., issues of too much and too little sediment, before considering relevant sediment management options and requirements, and also the possible effects of global environmental change (FÖRSTNER & OWENS 2007). The sediment budget concept offers considerable potential for sediment management and should form part of the early stages of a river basin plan for sediment management (see OWENS 2005).

The effects of global environmental change on sediment fluxes in river basins are at the centre of numerous research programmes and initiatives, including the International Sedimentation Initiative (ISI), that has been launched by the United Nations Educational, Scientific, and Cultural Organization (UNESCO), as a major activity of the International Hydrological Programme (IHP; www.unesco.org/water/ihp).

3 Hydraulics – key factor for contaminated sediment in river basins

Sediment physical parameters are the basis of any risk assessment both on local and river basin scales. In the decision process, sediment stability should be considered a subset of an overall risk-management framework, using a tiered approach, which is characterized by a progressive increase in complexity – e. g., definition of key elements at the site, regional geomorphology to understand the sensitivity of the site to flood-associated flows, and definition of needs for sediment sampling, acoustic surveying and current measurements.

With respect to sediment-associated contaminants, questions that should be asked during selection of management options include: (i) Is the site erosive or depositional? (ii) Will management options change that, and how will that impact other sites downstream? (iii) Can the normal sedimentation process in the area solve the problem through burial and mixing? Or as the principle question: Should we wait for the natural recovery mechanisms to reduce the risk due to sedimentation, degradation or other natural attenuation processes, or does the situation require removal of the contaminated sediments?

The quantification of flow rates including the transport of particle aggregates, microorganisms as well as dissolved and adsorbed substances requires an integration of various experimental techniques (flumes, turbulence columns, erosion chambers), to study the combined effects of sediment processes during resuspension, transport and deposition, and to describe these processes by models on different scales for the determination of hydrodynamic, chemical and biological parameters.

Two examples of integrated programmes are presented here: (3.1) The German SEDYMO-programme, with special emphasis on fine-grained sediments and comprising a typical set of factors commonly influencing solution/solid equilibrium conditions, and (3.2) the U.S. programme on sediment remediation with its focus on science-based "soft" technologies such as monitored natural recovery and *in-situ* capping.

3.1 Hydrodynamic factors in integrated river basin strategies – SEDYMO

Both for establishing sediment-related quality objectives and for developing and implementing technical problem solutions, practical process-based knowledge is needed that uses a wide range of simulation techniques and models in different spatial and temporal scales. Analytical and numerical models are indispensable for both connecting and integrating the interdisciplinary study of individual processes and for transferring the findings from laboratory experiments to a natural aquatic system where processes take place on extremely variable scales both in space and time.

In the German SEDYMO-programme ("Fine sediment dynamics and pollutant mobility in rivers") examples are the delayed release of metals from resuspended anoxic sediments

(SIEPMANN et al. 2007) and the relationship between sediment-associated phosphorous entrainment rates and bed shear velocities (KLEEBERG et al. 2007). Empirical methods used to assess the erosion characteristics of a cohesive deposit indicate that despite the small size of most of the available experimental apparatus, the resulting flows represent a reasonable simulation of the flow conditions at the sediment-water interface. The programme included two subprojects using sediment stability tests which could bridge the gap between laboratory and field ("Triad System", GERBERSDORF et al. 2007; "Microcosm/Hot film anemometer", MÜLLER et al. 2007). The influence of hydrodynamics on sediment ecotoxicity was studied by HOLLERT et al. (2007).

The position of integrated process studies, between ecotoxicological risk assessment and remediation technologies in the management of aquatic sediments and dredged materials is presented in Figure 2, which also explains the position of this multidisciplinary research programme in the context of the WFD and other intregrated river basin approaches. Strategies against chemical pollution of surface waters (WFD article 16) – i. e. implementation of monitoring programmes until 2006 and establishment of the programme of measures until 2009 – have to consider sediment quality (and quantity) at the catchment scale. With respect to the latter date, the first step – screening of all generic sources that can result in releases of priority substances and priority hazardous substances – will already include an assessment of the specific source/pathway of 'historical pollution from sediment'.

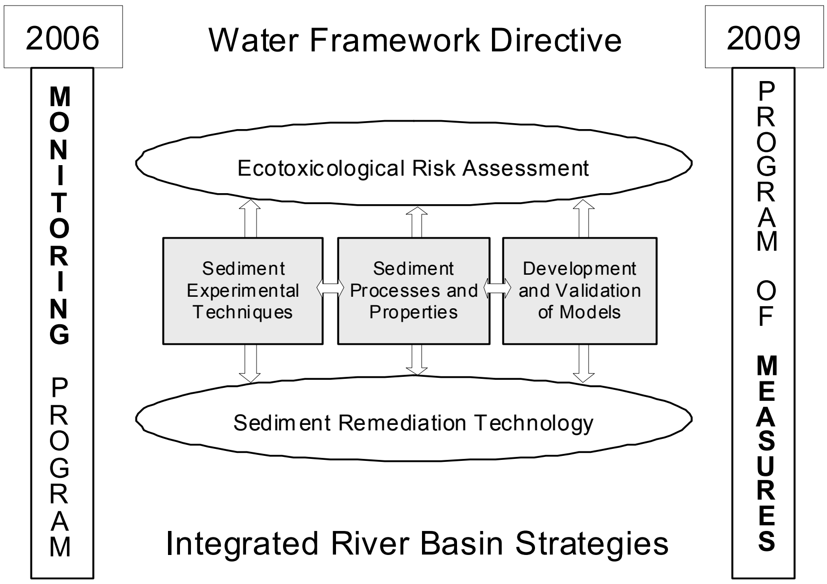

Figure 2: Embedding of themes and aims of the Priority Research Project SEDYMO in the EU Framework Directive and other integrated river basin strategies

3.2 United States sediment remediation programme – parameter lists

The final management strategy, apart from economic and social factors, mainly involves engineering elements such as technical feasibility, contaminant reduction, and permanence of remedial options like capping, *in-situ* treatment, and dredging and disposal. A critical review of recent developments was made by FÖRSTNER & APITZ (2007) on the basis of the presentations at the 4th Battelle Conference of Sediment Remediation (FOOTE & DURRELL 2007).

tions at the 4th Battelle Conference of Sediment Remediation (FOOTE & DURRELL 2007). Actually, the United States have a leading position due to the efforts under the Superfund Act (U.S. EPA 2005). An increasing use of comparative risk assessments considers all risks of a remedial option; these assessments include a wide spectrum of methods, including typical procedures for studying physical sediment stability (Figure 3, after WENNING et al. 2007), and range from initial site analysis up to long-term monitoring of technological performance and ecological effects. Biological monitoring after cap construction includes monitoring of the benthic community that may recolonize the capped site and the bioturbation behaviour of bottom-dwelling organisms. Natural attenuation effects can be monitored using biota recovery, e. g., benthic community size and/or diversity (U.S. EPA 2005).

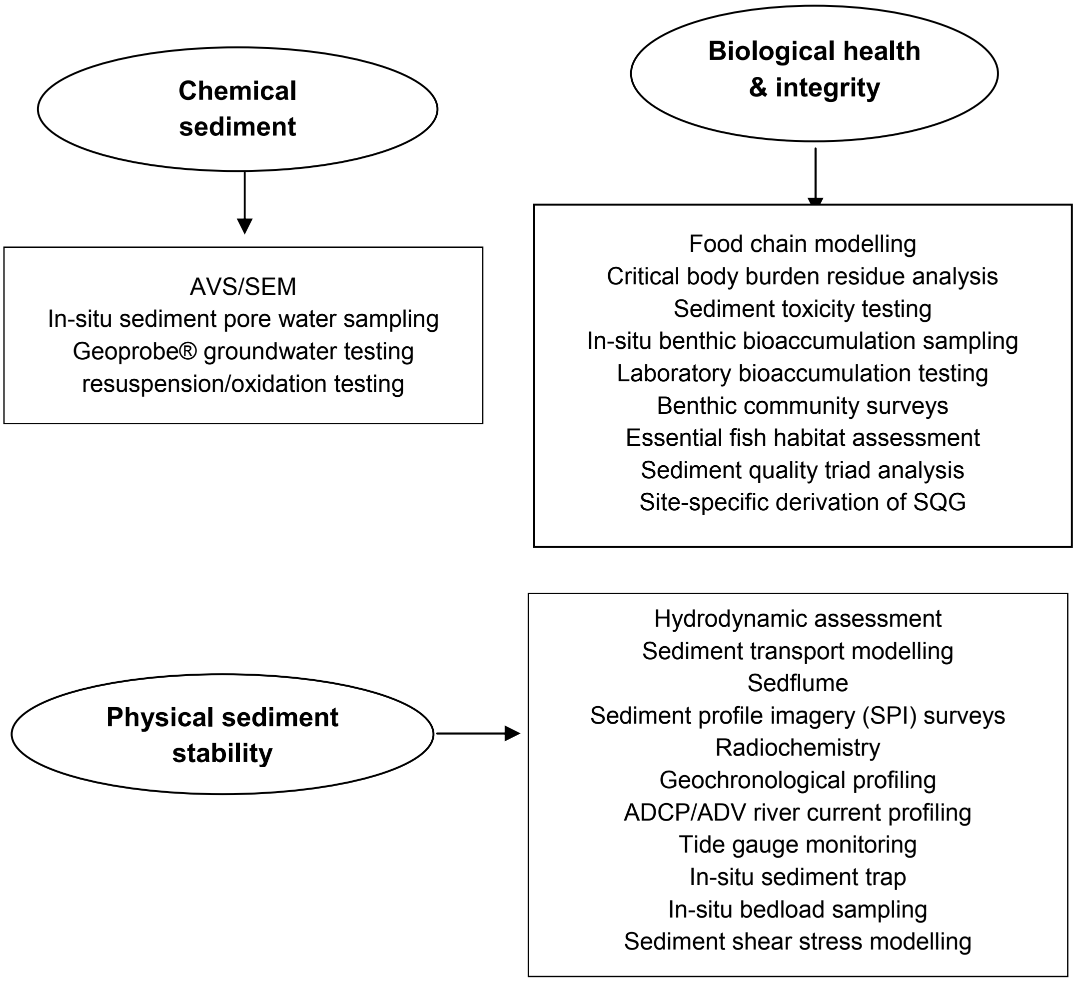

Figure 3: Studies contributing to risk analysis (after a design of ENVIRON, WENNING et al. 2007)

4 From monitoring to measures

Disposal and re-suspension (erosion) of sediment occur reversibly depending on hydraulic conditions, in particular current velocity. These hydraulic conditions may vary within a short period of time and distance. Despite these obvious drawbacks, in particular the inhomogeneous character of sediment layers and sediment/SPM grain size – particulate matter can be the preferred medium in a wide spectrum of assessment objectives and programmes (THOMAS & MEYBECK 1992; the objectives are listed in increasing order of complexity, with each step requiring more sampling and measurement):

> to assess the present concentrations of substances including pollutants found in the particulate matter and their variations in time and in space (*basic surveys*);

> to estimate past pollution levels and events (e. g., for the last 100 years) from the analysis of deposited sediments (*environmental archive*);

> to determine the bioavailability of substances or pollutants during the transport of particulate matter through rivers and reservoirs (*bioavailability assessment*);

> to determine the fluxes of substances and pollutants to major water bodies (i. e., regional seas, oceans) (*flux monitoring*); and

> to establish trends in concentrations and fluxes of substances/pollutants (*trend monitoring*).

4.1 Monitoring historical contaminated sediments: Pragmatic approch

Historical pollution from sediments was studied from the Rhine Basin (2004, for Port of Rotterdam) and from the Elbe River basin. The basis was the 3-step approach of HEISE & FÖRSTNER (2006): (1) Substances of Concern, (2) Areas of Concern and (3) Areas of Risk. The example of the Rhine River provided favourable conditions for the interpretation of basin-wide data:

(i) full coverage of flood events by sampling and analysis of suspended particulate matter and pollutant loads,

(ii) target levels for harbour authorities, to decide whether dredged material from harbour goes to the sea or to a confined disposal site,

(iii) the most critical pollutant hexachlorobenzene occurs in the main river and, therefore, the most dominant effect downstream is dilution, and

(iv) additional information on tracer substances, models and experimental studies on erosion and resuspension under flood conditions.

In the Rhine River, an increased risk is observed, if the flood wave is restricted to a limited area upstream, and hence normal discharges in the tributaries downstream of this area do not lead to major dilution effects. This situation can take place during spring and early summer, when snow melting increases the discharge in the main river and exposes typical hexachlorobenzene (HCB) contaminated material in the barrages of the Higher and Upper Rhine. More than 500 km downstream, at the border to The Netherlands, the concentration curves of HCB widely follows the upstream water discharge curves. The concentrations of HCB are significantly higher than the CTT (Chemistry-Toxicity Test) action levels for this pollutant, set by the Dutch authorities to relocate dredged material from Rotterdam harbour to the North Sea.

4.2 Sediment quality assessment in the European Water Framework Directive

In theory, sediment issues have developed reasonably under the European Water Framework Directive following an intial underestimation by the water authorities and regulatory bodies of the practical problems with this medium (FÖRSTNER 2002). Following the advise from the EAF, the Expert Group on Analysis and Monitoring of Priority Substances proposed not to establish quality standards for biota and sediment at this stage, but to designate monitoring requirements to assess the compliance with the no deterioration objective of the WFD and to assess long term impacts of anthropogenic pressures. The controversial EQS-discussion on sediments was somewhat disarmed by SedNet, the European Sediment Research Network, at the SedNet Round Table in Venice, November 2006; definitions in both subject areas – monitoring and measures – were were adopted (NETZBAND et al. 2007): "Environmental Quality Standards should only be regarded as high-level screening values as a start of diagnostics, using different lines of evidence, and linking sediment state to impacts" and "for certain measures target values and a good understanding of the system are necessary". These conclusions are in line with the concensus of other international expert bodies, as summarized in WENNING et al. (2005).

4.3 Uncertainties during monitoring of contaminated sediments

With respect to data quality control in water, an European thematic network METROPOLIS has identified typical problem areas, for example: (i) A too high level of uncertainty of the selected data may endanger the whole decision-making process and (ii) lack of traceability. The concept of traceability implies that measurement data are linked to stated references through an unbroken chain of comparison, all with stated uncertainties (QUEVAUVILLER 2004). From a practical view, the traceability concept for quality control of chemical sediment analysis comprises three categories of investigations (Figure 4; FÖRSTNER & HEISE 2006):

> *Memory effect*, mainly in dated sediment cores from lakes, reservoirs and marine basins, as historical records reflecting variations of pollution intensities in a catchment area. As regards the traceability concept, the basic sequence of measurements consists of three steps, which can be considered as an unbroken chain of comparisons.

> *Basic characterization*, i. e., sediment as ecological, social and economic value, as an essential part of the aquatic ecosystem by forming a variety of habitats and environments. A system approach is needed comprising biotests and effect-integrating measurements due to the inefficiency of chemical analysis in the assessment of complex contamination.

> *Secondary source*, mobilisation of contaminated particles and release of contaminants after natural or artificial re-suspension of sediments. On a river-basin scale, i. e., when applied in a conceptual river basin model (see above), chemical and ecological information need a strong basis of sediment quantity data. In a dynamic system, this assessment should include not just those materials that are currently sediments, but also materials such as soils, mine tailings, etc. that can reasonably be expected to become part of the sediment cycle during the lifetime of a management approach (APITZ & WHITE 2003).

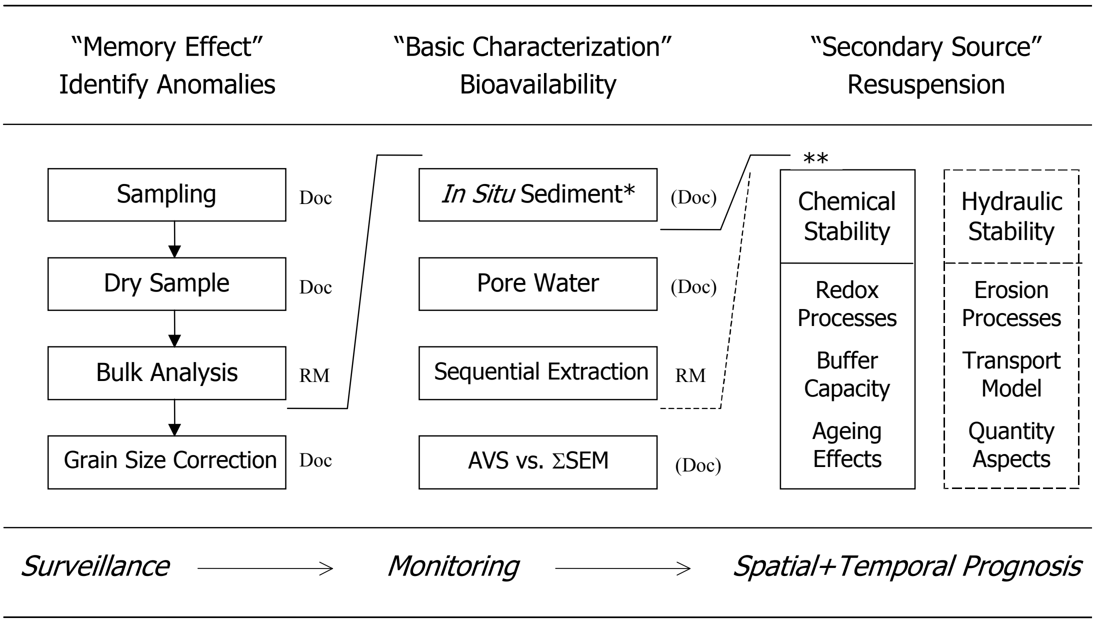

Figure 4: Schematic overview on traceability aspects of chemical sediment analysis (FÖRSTNER & HEISE 2006). RM = Reference Material; Doc = Documented Procedure; AVS/-ΣSEM = Acid Volatile Sulfide/Sum of Simultaneously Extractable Metals; *Wet Sample: Sub-sampling for tests under oxygen-free atmosphere (pore water, sequential extraction, etc.).

4.4 Basin-wide *in-situ* remedial options: examples from the Elbe River

Recent developments in 'soft' (geochemical and biological) techniques on contaminated soils and sediments, both with respect to policy aspects as to technical developments have led to a stimulation of *in-situ* remediation options. 'Geochemical engineering' applies principles such as stabilization, solidification, and other forms of long-term, self-containing barriers to determine the mobilization and biological availability of critical pollutants. Figure 5 gives examples for such techniques on a catchment scale.

Predominantly in the upper and middle course of river systems, sediments are affected by contamination sources like wastewater, mine water from flooded mines and atmospheric deposition. Measures at the source are particularly important and may include an improvement of traditional wastewater purification, but also more approaches for *in-situ* treatment of highly contaminated effluents such as introducing active barriers (fly ash, red mud, tree bark, etc.) into ore mines to prevent heavy metal dispersion during flooding (ZOUMIS et al. 2000).

From an initial example of the Spittelwasser, a 60 km² flood plain of the upper Elbe River, a complex *in-situ* remedial demonstration, utilizing a mix of technologies was chosen by the organisers of the international conference ConSoil 2000 for a case comparison. Four expert teams from Denmark, Germany, the Netherlands and the UK were invited to participate in this Case Study. Evaluation of the plan was done by members of the networks of NICOLE (Network for Industrially Contaminated Land) and CLARINET (Contaminated Land Rehabilitation Network), but this innovative programme, though positively reviewed on a technical basis, has yet to be funded (APITZ 2008).

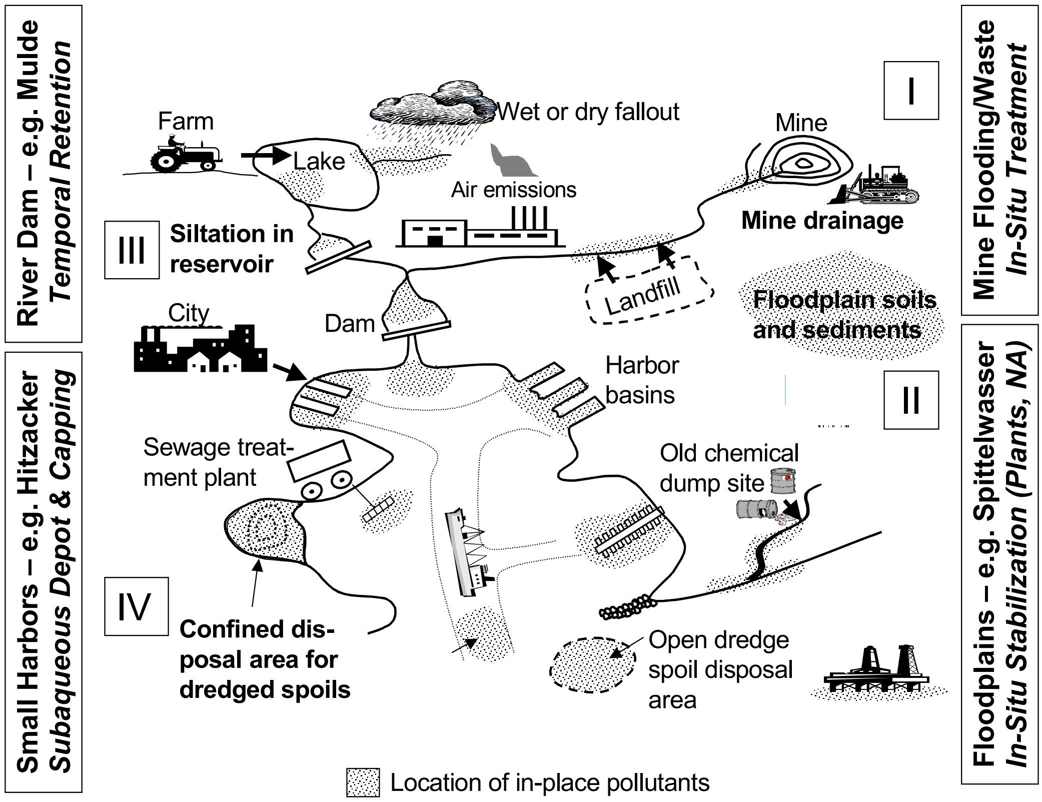

Figure 5: Sediment contamination in a river catchment area and proposals for treatment methodologies in the Elbe river basin (see text)

Application of a combined sub-aquatic depot and active capping technology can be considered for small yachting harbors. For the Hitzacker/Elbe harbor site, a draft approval has been made which involves the excavation of approx. 10,000 m³ fine grained, polluted sediments from the harbor area and their sub-aquatic deposition close to the site, in a communication channel between the Elbe River and the harbor. Active capping of the sediment depot will include natural zeolite additives and monitoring of the site will be performed using dialysis sampler and diffusional gradient technique probes (JACOBS 2003). Although this approach of was first proposed in Europe (JACOBS & FÖRSTNER 1999), to date, the Hitzacker/Elbe demonstration study, though carefully reviewed, has not been accepted for funding.

5 Outlook: Learning from *in-situ* sediment remediation in the U.S.

In a global perspective, the present situation of sediment management on a regional scale can be characterized by conceptual advantages in Europe, originating from the step-wise implementation of the basin-wide Water Framework Directive, and by the enormous technological and strategic experience assembled in the United States during recent years. Here, in particular, an increasing use of comparative risk assessments (CRA) that consider all risks of a remedial option, including those of removal, residuals, treatment, transport and disposal, provides a growing body of evidence which suggests that sediment removal can at times result in more human health risk and ecological damage, or, after great expense, not show measurable ecological improvement (WENNING et al. 2007).

Based on the U.S. EPA's "Contaminated Sediment Remediation Guidance for Hazardous Waste Sites (U.S. EPA 2005), the currently mature and available management strategies for contaminated sediments (not dredged material) are dredging, capping, and monitored natural recovery (MNR). In 2004, the U.S. EPA decided to take action to clean up contaminated sediment at approximately 140 sites; capping, either alone or in combination with removal and/or MNR, is planned or has been implemented at about 40 sediment remediation projects in the United States, whereas MNR as a primary remedy, or in combination, is a component of about 28 projects in the United States. In spite of the above, however, both capping and MNR continue to be "a harder sell" as the remedy of choice for regulatory agencies and the public because the contaminants are left in place (ZELLER & CUSHING 2006; Table 2).

Table 2
Some site characteristics and conditions especially conducive to particular innovative remedial approaches for contaminated sediment (after U.S. EPA Sediment Remediation Guidance 2005)

Characteristics	Monitored Natural Recovery	*In-situ* Capping
General Site Characteristics	• Anticipated land uses compatible • NR processes continue at rates to destroy or reduce pollutants	• Cap materias available at site • Infrastructure compatible • Water depth adequate for uses
Human and Ecological Environment	• Expected human exposure is low • Sites includes environment too sensitive for capping or dredging	• Human exposure is substantial • Long-term risk reduction vs habitat disruption; new habitat?
Hydrodynamic Conditions	• Deposition of sediment occurs in the areas of contamination; hydrodynamics not to compromise NR	• Hydrodynamic conditions not likely to compromise cap or can be accommodated
Sediment Characteristics	• Sediment is resistant to resuspension (cohesive or well-armoured)	• Sediment sufficient strength to support cap (density, low H_2O)
Contaminant Characteristics	• Contaminants ready biodegrade or transform to less toxic forms • Have low ability to bioaccumulate	• Contamination covers contiguous areas (to simply capping) • Low rates of flux through cap

In Europe, although tasked to examine all aspects of contaminated sediment management at the river-basin scale, the European demand-driven Sediment Research Network (SedNet), after a 3-year programme, primarily examined *ex-situ* sediment management strategies at depth in its summary reports (BORTONE 2006). Whilst to a certain extent this reflects a perceived lack of a "market" for *in-situ* management in Europe, the European Commission has stated that decisions and policies should be continuously evaluated in the light of emerging science and experience, and, where possible, rigorous science-based risk evaluation should take the place of the application of conservative safety factors (APITZ 2008).

Generally, in order to give *in-situ* remedial options such as *in-situ* capping or MNR a real chance, a shift of emphasis is needed towards the communication of results from the analyses of multiple lines of evidence, e. g., by examining the potential impacts of large, low-probability events or combination of probabilities on exposure and risk, and the associated uncertainties (BOHLEN & ERICKSON 2005). The role of biota, in controlling contaminant fate, and the factors influencing bioavailability of contaminants to various receptors, are all important subjects if site-specific characteristics are to inform risk-based assessment and management.

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Sediment assessment from a user‘s perspective

Axel Netzband

Zusammenfassung

Regelmäßige Bewertungen der Sedimentqualität sind im Hamburger Hafen im Rahmen des Baggergutmanagement genauso erforderlich wie überall dort, wo Sedimente gebaggert und untergebracht werden müssen. Das gegenwärtige Vorgehen weist allerdings Mängel auf, die zu den Anforderungen des Baggergutmanagements und den Unterbringungsoptionen im Widerspruch stehen. Deshalb wird nun ein neuer Ansatz vorgestellt, der sich den Anforderungen der neuen europäischen Vorschriften anpassen lässt und der eine Verbindung zur Sanierung der Elbe herstellen kann.

Auch in der Zukunft bleibt die Notwendigkeit chemischer Analysen für die WRRL und für andere Anforderungen bestehen, besonders für die Nachverfolgbarkeit von Verunreinigungen. Prinzipiell können ökotoxikologische Methoden die Unzulänglichkeiten der chemischen Analysen ausgleichen bzw. zu weiterführenden Untersuchungen Anlass geben. Bei ihrer Anwendung im Baggergutmanagement sind jedoch einige Fragen zu beantworten: Was sagt eine im Test beobachtete Wirkung über die Risiken an der Unterbringungsstelle aus? Was bedeutet dies für den ökologischen Status eines speziellen Gewässers gemäß WRRL? Kann ein einziger Test das alleinige Kriterium sein?

Summary

Regular assessment of sediment quality is necessary for dredged material management in the Port of Hamburg, like elsewhere where dredged sediments have to be managed. But the present course of action has shortcomings conflicting with requirements of dredging management and disposal options. Therefore a new approach is being presented. It can also be integrated into requirements of new EC regulations and pose a link to restoration of the Elbe.

Also in the future chemical analyses will remain necessary for WFD and other requirements, especially for contamination traceability. Essentially ecotoxicological methods can cover the shortcomings of chemical analyses or trigger further examination. Their application for dredged material management has to answer questions. What does a test effect tell about risks a the placement site, what does it mean for the specific water body status (WFD), and can one test be a “one out – all out” criteria?

1 Introduction

Recurring maintenance dredging is necessary in most ports and marine waterways. In the North Sea region most big ports are situated in estuaries or at the mouth of large rivers. In these estuaries 10 to 20 Million m^3 have to be dredged annually to maintain water depths for safe navigation. International conventions and national regulations require proper assessment of the disposal of these dredged sediments when they are brought back to the aquatic environment. Central element of this assessment is the chemical and ecotoxicological description.

This paper discusses the specific situation in the Port of Hamburg and the sediment assessment resulting in necessary management decisions in regular Maintenance Dredging. It does deal neither with Capital nor with Remedial Dredging – which is done as well, but which require different approaches. Another starting point is that disposal options have been thoroughly assessed through an Environmental Impact Assessment (EIA etc.).

2 Sediment transport

The Port of Hamburg is situated 100 km away from the sea at the upper end of the Elbe estuary. Annually roughly 6 Million m^3 had to be dredged in the last years; another 15 Million m^3 have to be dredged in the fairway maintained by the Federal Waterways Administration. Most of this sediment stems from the sea, being pumped into the estuary by the tide. These sediments are coarser and only very slightly contaminated. The river brings in fine grained sediments, which still are contaminated to a certain extent. Both volume flows mix in the estuary. Sedimentation occurs where flow velocities are low, like it is the case in harbour basins, for example.

Suspended matter transport in an estuary is very complex. General patterns are well understood, but in a large estuary, like the one of the Elbe, a balance of overall transports with prediction of sedimentation (and erosion) rates depending on natural variations and changing hydromorphology can only be estimated. Recently this has been described by KAPPENBERG & FANGER (2007).

The suspended matter load from upstream, passing the weir at Geesthacht, amounts to about 600,000 Tonnes/year. For example in the year 2006 (river discharge about average) 3.5 Million Tonnes dry matter had to be dredged in the Port, roughly 50/50 sand and silt. 400,000 Tonnes silt and 200,000 Tonnes sand had been taken out of the river to be disposed on land, mainly because of contamination of the silty material. These few figures give an estimation of relative loads. They also show that the Port is relieving the North Sea significantly from contamination input, stemming from upstream regions.

Most sedimentation occurs in the harbour basins. Figure 1 shows a typical sedimentation pattern in one of the basins. Here sedimentation can be up to 5 m/year; sometimes rates of 75 cm/month are possible. Because of a natural eddy current forming at the basin entrance here sedimentation rates are highest.

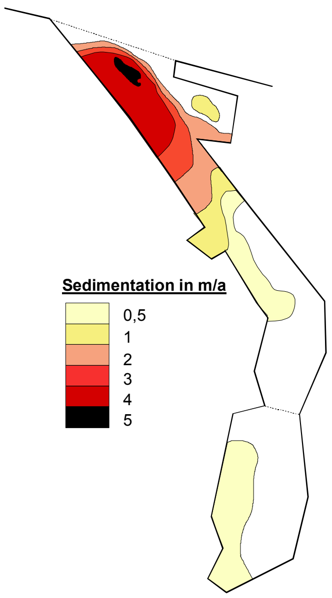


Figure 1
Sedimentation rates in the Köhlfleet basin.
(CHRISTIANSEN & HAAR 1996)

This sedimentation can rapidly lead to restrictions for vessal navigation. Figure 2 shows that water depths underneath a vessel can be less than 1 m, indicating an immediate need for dredging.

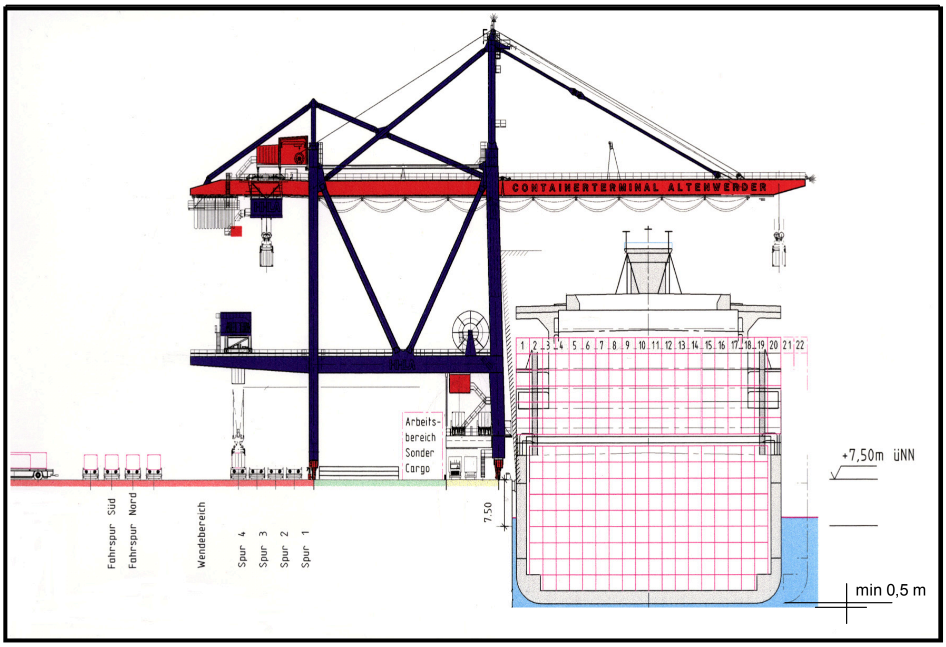


Figure 2: Schematic of water depths at a berthing facility.

Sedimentation in the Port is mainly driven by river discharge: When the discharge is high sedimentation is low, and vice versa. This is nearly impossible to predict, because it is mainly dependent on the rainfall in the whole Elbe catchment basin. Thus the sedimentation amount can vary by some Million m^3/year. This makes planning of necessary dredging operations very demanding.

3 Dredging

Sedimentation and navigation requirements lead to dredging needs. It becomes evident from the above that dredging may be needed at the same place in the Port several times a year. For disposal of the dredged sediments basically 2 options exist – land or water. Due to contamination of sediments 1.2 Million m^3/year are disposed of on land. Another roughly 5 Million m^3 are placed in the water, either downstream of the Port or in the North Sea. This makes testing and assessment a yes/no decision for either option. This decision is very complex and bears risks in several respects.

Equipment for relocation are trailing suction hopper dredgers, with a capacity of 2,000 m^3 for short distance transport and 10,000 m^3 for sailing to the North Sea placement site. These ships work on a contract base which requires a tender procedure. The world market for these vessels is under great pressure due to requirements in the Middle and Far East. Especially the larger hopper dredgers require a lead time of more than half a year. This means that they have to be ordered when the sediments they shall dredge do not even exist, not to name the amount. Costs are significantly above 5 €/m^3. Still this is much less costly than land disposal, which presently costs about 32 €/m^3.

So in the assessment of sediment quality lie several risks:

- For the environment: Do the sediments placed in the water pose a threat to ecology?
- For operation: Will there be the necessary equipment when it is needed? – A hopper which is there but has no sediments to dredge is expensive; no hopper but sediments is a threat to Port operation.
- For finances: The total yearly financial needs amount to many 10 Million Euros, this has to be minimised as possible

The environmental alternative to the ecological risks of open water placement is safe land disposal. This is costly and limited, and it takes a long time to develop. Suitable sites have to be found, fierce public opposition is preassigned.

In practical terms short term reversal is very limited. When a hopper dredger has been ordered it will become very costly to change its task. This means that well-based decisions have to be made well in advance, encompassing an assessment of all inherent scientific, political, financial, operational, and societal aspects.

4 Sediment assessment

Proper sediment assessment is the clue to management options ("Water or Land") both in terms of short term management decisions as well as the development of new options. Here the emphasis is put on the former. In our case assessment is based both on chemical parameters and on ecotoxicological tests.

Concerning chemical contamination mercury can be taken as an example. It was the main problem parameter when the Hamburg Dredged Material Concept was developed 25 years ago. Figure 3 shows its development over the last 24 years at a measuring point upstream the

Port of Hamburg. Also contamination of sediments in the Port area is well examined, over the years many 100 samples were taken. Figure 4 shows mercury in sediments foreseen for open water placement.

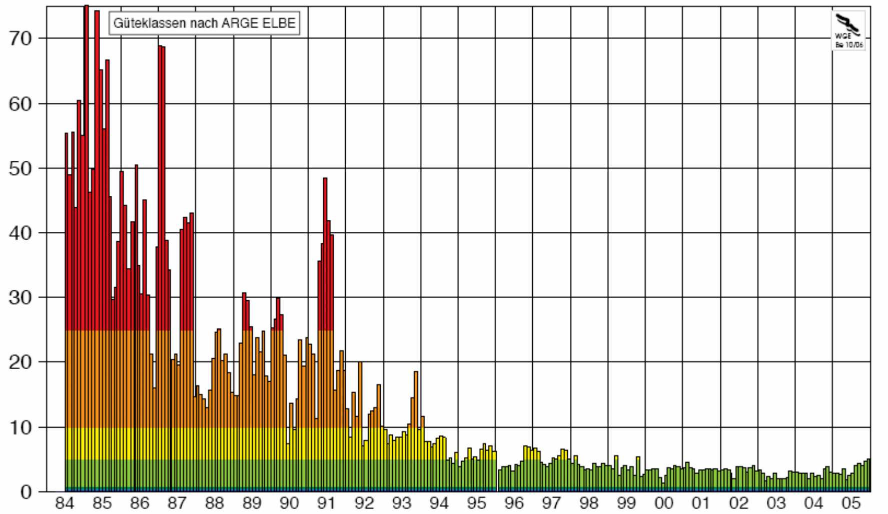


Figure 3: Mercury in fine grained fresh Elbe sediments at Schnackenburg, monthly samples. (Source: Wassergütestelle Elbe der ARGE Elbe)

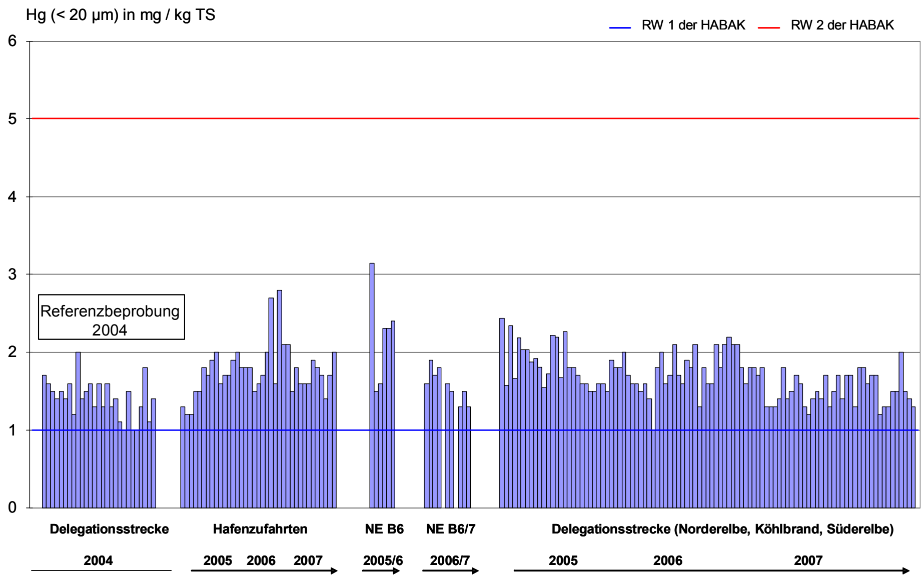


Figure 4: Mercury in sediments. Blue/red line are lower and upper HABAK values

From Figure 3 a steady development over the last decades becomes clear. Although the situation dramatically improved still target values are not reached yet. As improvement is now only very slow this elevated contamination may continue for a longer time. Figure 4 demonstrates that both over time and area variation in the values is only limited and lies in between the lower and upper values of the German HABAK regulations (BfG 1999) for dredged material management of the Federal Waterways Administration.

Figure 4 also shows that single values distinctly above the normal or anticipated values do occur. Reasons can be manifold. Because a hopper dredger is dredging a dredging field as a whole in several turns at latest here different “sediment samples” will be mixed. This means for assessment averaging of close samples makes much more sense than considering only single samples.

Compared with chemical testing the picture is different for ecotoxicological testing. Also here nowadays several hundreds of results exist. Altogether they show that Elbe sediments still do have toxicological responses in some of the tests applied. At the same time this does not relate to any of the measured contaminants; where the highest TBT contamination occurs the tests do not show specific responses, for example. It seems that they reflect a specific Elbe characteristic, and research is undertaken to identify the cause of this effect.

More problematic is the effect on short term dredged material management. While, as stated before, chemical contamination to a certain extent can be foreseen in a certain range this is different with bioassays. Especially one test with freshwater algae (*Desmodesmus subspicatus*) shows a high degree of spatial and temporal variability in the test results which makes management sometimes a Russian roulette. In contrast to the HABAK regulation, the permit given by the authorities for North Sea disposal does not allow relocation in case of exceedance of a certain value in one of the bioassays, irrespective of other results in the same sample. Several times different samples showed very different results in one sampling campaign in one defined dredging field. This was not reflected by other parameters nor could it be explained by sedimentation patterns or other reasons. Even control samples taken shortly later at the same place where the exceedance occured did show a different picture – much lesser contamination than before. This is of high risk for maintaining the water depths, and does not seem to protect the environment in a proper way. It is felt that an overall assessment should be developed.

5 Sediment assessment and River Basin Management

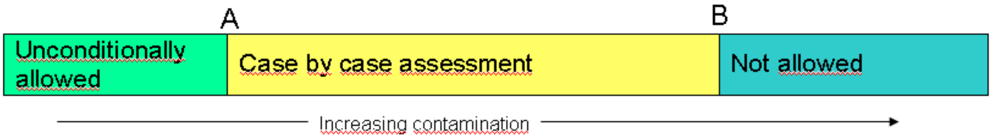
The new EC Directive on Environmental Quality Standards will require “Member States should monitor sediment and biota, as appropriate, at an adequate frequency to provide sufficient data for a reliable long-term trend analysis of those priority substances that tend to accumulate in sediment and/or biota.” And also the new EC Waste Directive states “Sediments relocated inside surface waters shall be excluded from the scope of this Directive if it is proved that the sediments are non-hazardous.” This shows that Dredged Material Management as it is now should be integrated into a larger River Basin Sediment Management.

In the Hamburg and Elbe case it is evident that contamination problems can only – and have to be – solved at source, which in this case means in the whole river basin. Because it serves the overall environment and the river community decisions on dredged material management should be based in this context. Regular survey of contamination development can then also serve as feed back for river restoration measures.

Assessment of sediments for dredged material management at the same time is also an assessment of the specific water body and should be linked to River Basin Management under the Water Framework Directive.

Thus chemical parameters to be measured should comprise especially those relevant for the specific river and therefore need to be defined by the river community. Because in any case this will be only a small selection of the “chemical zoo” appropriate ecotoxicological tests should be applied as well. Both have to be integrated into an assessment method which also takes into account the requirements of dredged material management, as described above. This means at least that all tests and results have to be assessed in a holistic manner.

A suggestion for decisions for dredged material options as an element of River Basin Management based on chemical and exotoxicological measurements could be



If the result of the above mentioned assessment is above B open water placement is not an option. Value A will be mainly scientifically derived from an environmentally desirable point of view and thus be something like a target value. Value B will also have to consider the existing situation, management options, political and economical needs and constraints. It is only valid for a transition time and should be linked to remediation measures. It will have to be agreed on a broader basis and needs regular revisal. Thus it will be a benchmark for river restoration, too.

When values are in the green section “the world is in good order”. When being blue it is a clear need for river restoration and a need for confined disposal of dredged sediments. The methods and the assessment for a decision on sediment options have to be

> reliable – meaning that test results reflect what the are meant to measure

> robust – the method or system has to balance short term changes and variations

> representative – the result has to reflect the overall situation of the specific area

In the Port of Hamburg the large amounts are being dredged in some few, always the same areas with very little local emission influence and thus reflecting the situation of the Elbe river in Hamburg. Automatic sampling stations directly upstream of the Port and in the Port itself take monthly samples of fresh sediments. These data could serve as an early warning system, possibly also in conjunction with appropriate ecotoxicological tests.

On this basis, also considering the practical options of the daily management, it seems more appropriate to do a comprehensive sampling campaign every 2 or 3 years and, based on this, define areas for disposal options. Thus short term assessment decisions with their shortcomings could be avoided, or only applied case wise for control when necessary.

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Projects:
Effluent treatment from dredged material disposal sites
Treatment and land disposal of dredged material
Open water placement of sediments
Several national and international working groups

The Chemical Monitoring Activity under the Water Framework Directive

Mario Carere

Zusammenfassung

Die Wasser-Rahmenrichtlinie (WRRL) hat das Ziel, bis zum Jahr 2015 in allen europäischen Oberflächengewässern guten chemischen und ökologischen Status zu erreichen.

Der gute chemische Status wird durch die Einhaltung der auf europäischer Ebene definierten Umweltqualitätsstandards für die Konzentrationen prioritärer Substanzen repräsentiert. In diesem Zusammenhang stellt die Veröffentlichung der Direktive 2008/105/EC des Europäischen Parlaments und des Rats zu Umweltqualitätsstandards auf dem Gebiet der Wasserpolitik einen entscheidenden Meilenstein dar.

Für die übrigen Stoffe wählen die Mitgliedsstaaten aus der Liste der chemischen Parameter diejenigen aus, die auf der Ebene des Flusseinzugsgebiets relevant sind und die überwacht werden sollen. Diese Auswahl sollte auf Daten der Umweltüberwachung und auf Belastungsanalysen beruhen. Der Überwachungsplan sollte die Analyse der Chemikalien in der Wassersäule, im Sediment und in den Biota auf der Grundlage ihrer biologischen, chemischen und physikalischen Eigenschaften umfassen.

Zu diesem Zweck wurde eine neue Aktivität, die sogenannte “Chemical Monitoring Activity”, unter der Common Implementation Strategy (CIS) eingerichtet, um Experten für die Überwachung der Oberflächengewässer und des Grundwassers zusammenzubringen und die technischen und methodischen Verfahren der Überwachungstätigkeiten abzustimmen.

Abstract

The Water Framework Directive (WFD) has the aim to achieve good chemical and ecological status in all European surface water bodies by 2015.

The good chemical status is represented by the compliance of the concentrations of priority substances with the environmental quality standard defined at European level. In this context the publication of Directive 2008/105/EC of the European Parliament and of the Council on environmental quality standards in the field of water policy represents a key milestone.

For the other substances the Member States should select the list of chemical parameters, relevant at river basin level, for which monitoring should be put in place; the selection should

be based on monitoring data and on analysis of pressure. The monitoring plan should include the analysis of chemical substances in column waters, sediment and biota on the basis of their biological, chemical and physical properties.

For these purposes a new activity, called "Chemical Monitoring Activity" has been put in place under the Common Implementation Strategy (CIS), bringing together experts on surface and ground water monitoring in order to ensure an harmonisation of technical and methodological procedures for the monitoring activity.

1 Introduction

The key milestone for the implementation of WFD is the setting of monitoring programme for surface and groundwaters; the objective is to establish a coherent and comprehensive overview of water "status" within each river basin district and it concerns surface waters (rivers, lakes, transitional, coastal and territorial waters) groundwaters and protected areas (like for example areas designed for drinking water purposes or area designed in the context of Habitat Directive).

In the context of WFD there are 3 types of monitoring for which chemical measurements are the core of the activity: <u>surveillance monitoring</u> that should cover all water bodies and should be made at least within every river basin management plan, the <u>operational monitoring</u> specific designed for water bodies at risk and the <u>investigative monitoring</u> specific designed for water bodies in which are not clear the causes of failing of the environmental objectives or in which accidents have been occurred.

The monitoring data represent the link between the evaluation of the pressures and the impact that this pressure generates on waterbodies: The chemical measurements are fundamental tools in terms of prevention because without the understanding of the status of the environment every policy response can under- or over-estimate the pollution risk for the water environment.

2 The Directive on Environmental Quality Standard and the role of sediment

After several years of technical and political discussions the Directive on environmental quality standards (EQS) for surface water priority substances has now been published.

The key components of the Directive are the setting of EQS for the water phase for 33 priority substances and for 8 dangerous substances derived from list I of the "dangerous substances directive" and the setting of EQS for the biota for hexachlorobenzene, mercury and hexachlorobutadiene.

In the Directive is foreseen also the identification of 2 new priority hazardous substances that have to be eliminated from all discharges, emissions and losses within 20 years from the publication of the directive and a list of new substances, mostly emerging compounds, for which the European Commission will do a review to evaluate their inclusion in the list of priority substances.

The Directive defines 2 types of environmental quality standard, the annual average and the maximum allowable concentration: The first is based mainly on chronic bioassay and should protect all trophic levels of the aquatic ecosystems from long-term effects, the second EQS, higher than the first, should protect from short-term effects due for example to illegal discharges or accidents and is infact based on acute ecotoxicological effects .

Table 1
Criteria for the derivation of environmental quality standard

Protection objectives	**Criteria**
Pelagic community – freshwaters	Acute and chronic bioassays – application of safety factors
Pelagic community – other surface waters	Acute and chronic bioassays – application of safety factors
Benthic Community	Equilibrium Partitioning Method
Top-predators	Use of NOAEL and mammals and birds diet – use of BCF or BMF
Human Health – drinking water consumption	Drinking water standard – removal treatment efficiency
Human Health – seafood consumption	Use of NOAEL and ADI (acceptable daily intake), use of BCF

NOAEL: No Observed Adverse Effect Level
BCF: Bioconcentration Factor
BMF: Biomagnification factor

The EQS are different between inland waters (rivers, lakes) and other waters (transitional, coastal and territorial waters).

The role of the sediment in the Directive is useful. Member States can derive EQS for sediment instead of water for specified substances; the EQS for sediment have to guarantee the same level of protection of the EQS derived for water.

Member States have to notify, through the Committee referred to in Article 21 of Directive 2000/60/EC, the substances for which EQS have been established, the reasons and basis for using this approach, the alternative EQS established, including the data and the methodology by which they were derived and the categories of surface water to which they would apply.

The derivation of EQS for sediment seems appropriate for specific water bodies like marine coastal waters in which sediment represents the final sink of many pollutants and at the same time the place in which most of the aquatic organisms live or have part of the life-cycle; in these waterbodies monitoring programmes in water column for some lipophilic compounds may be very misleading with regard to the real state of the environmental and chemical quality.

About sediment the Directive obliges Member States to arrange the long-term trend analysis of concentrations of those priority substances of Annex I of the Directive that tend to accumulate and shall determine the frequency of monitoring to provide sufficient data for a reliable long-term trend analysis.

Furthermore Member States shall establish an inventory, including maps, if available, of emissions, discharges and losses of all priority substances and pollutants listed in Part A of Annex I to the Directive for each river basin district or part of a river basin district lying within their territory including their concentrations in sediment and biota, as appropriate.

The Directive is related also to the chemical quality of the sediment matrix, but is it recognised from the International Scientific Community that the assessment of sediment quality should not be based only on chemical analysis, but should include also the use of bioassays for the effect assessment and the evaluation of ecological quality for the impact assessment.

The chemical criteria approach should be supported by bioassays, bioaccumulation tests and ecological analysis with the aim to define an integrated assessment of contaminated sediments and to evaluate better the toxic effects on the benthic organisms and the impacts on the aquatic ecosystems.

There is the need to include in the context of the CIS (Common Implementation Strategy) alternative monitoring tools like for example biomarker or bioassays that can represent a link between the evaluation of chemical and ecological status and can also be used in the context of the investigative monitoring.

3 The European Expert Group: Chemical Monitoring Activity

The key issues of the European Expert Group “Chemical Monitoring Activity” are the monitoring design and strategies in relation to compliance checking to chemical status and the elaboration of working documents including aspects of quality assurance.

The activity of the expert group CMA (Chemical Monitoring Activity) in particular consists in 3 sub-activities led by Member States or Stakeholder Organisations: The first sub-activity aims to develop monitoring guidance document, exchange best practices and recommendations on monitoring programme design (sampling, selection of monitoring points, frequency of monitoring, monitoring of diffuse sources) included sediment and biota. Within this sub-activity has been elaborated and approved the “Surface water monitoring guidance”in which, *inter alia*, are described technical procedures for a correct monitoring design. For 2009 is foreseen the elaboration of a guidance for sediment and biota monitoring.

In the context of this sub-activity field trials have been organised in the Po river basin and in the Danube river basin (Budapest) to test methods and to compare sampling, river water extract and standard solutions.

The second sub-activity aims to develop a common strategy for quality assurance and control of chemical monitoring data, in close connection with the progress of the EAQC-WISE (European Analytical Quality Control in support of the Water Framework Directive via the Water Information System for Europe) European project and development of a data flow quality concept in support of the chemical monitoring of surface and ground waters.

Under this sub-activity has been elaborated a Directive of the European Commission on Quality Assurance and Quality Control that establishes minimum performance criteria for methods of analysis to be applied by Member States when monitoring water chemical status, sediment and biota, as well as rules for demonstrating the quality of analytical results; the Directive obliges the Member States to ensure that all methods of analysis, including laboratory, field and on-line methods, used for the purposes of chemical monitoring programmes carried out under Directive 2000/60/EC are validated and documented in accordance with EN ISO/IEC-17025 standard.

The third sub-activity is related to the identification and evaluation of standardisation needs and appropriate actions and the establishment and proposal of list of new standards mandated to CEN; in particular the mandate to CEN for the development or improvement of standards in support of the WFD is related to the organochlorine pesticides, chloroalkanes, tributyltin compounds, pentabromodiphenylethers and PAH.

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A proposal for including an integrated sediments evaluation in the European Water Framework Directive

Maria J. Belzunce-Segarra, Angel Borja and Javier Franco

Zusammenfassung

Die Europäische Wasserrahmenrichtlinie (WRRL) formulierte das Konzept des "ökologischen Status" zur Bewertung der Gewässerqualität und löste damit in der wissenschaftlichen Gemeinschaft eine Entwicklung zur Definition dieses Begriffs aus, der den Zustand biologischer, hydromorphologischer and physikalisch-chemischer Qualitätselemente zugrunde legt. Dabei bezieht sich die physikalisch-chemische Qualität hauptsächlich auf das Wasser. Die Frage, ob auch Sedimente einbezogen werden sollten, wird diskutiert (CRANE 2003, BORJA et al. 2004b, BORJA & HEINRICH 2005).

Daneben richten die Mitgliedsstaaten Programme zum Überwachung der Gewässerqualität ein. Es gibt drei Typen von Monitoringprogrammen: Überwachungs-Monitoring, operatives Monitoring (beide im Routinebetrieb) und investigatives Monitoring (das fallweise erfolgt, wenn die Ursachen der Beeinträchtigung des ökologischen und chemischen Zustand unbekannt sind; BORJA et al. 2008b).

In diesem Beitrag wird eine Methodik vorgestellt, um

> Sedimente in die integrative Bewertung des ökologischen Status mariner Systeme einzubeziehen und

> Qualitätsbewertungen des Sediments für ein investigatives Monitoring anzuwenden.

Das vorgestellte Verfahren verbessert die Bestimmung der ökologischen Qualität durch eine Kombination mehrerer Parameter anstelle eines einzelnen Index. Am Beispiel einer Hochofenschlacke-Ablagerung an der baskischen Küste wird die Anwendung des TRIADE-Ansatzes (Kombination: chemische Analysen, akute Toxizitätsbewertung und biologische Parameter) vorgestellt und diskutiert.

1 Introduction

The European Water Framework Directive (WFD; Directive 2000/60/EC) has developed the concept of Ecological Status (ES) for the assessment of the quality of water bodies. Therefore, a development of new concepts, terminologies and tools to define such status has been generated within the scientific community. The ES is based upon the status of the biological, hydromorphological and physico-chemical quality elements. The physico-chemical quality is related mainly with waters but not for sediments. Hence, the necessity to integrate or not integrate sediments in the ES is discussed by scientists (CRANE 2003, BORJA et al. 2004b, BORJA & HEINRICH 2005).

On the other hand, Member States are establishing programmes for the monitoring of water bodies quality. These monitoring programmes can be of three types: surveillance monitoring; operational monitoring (both undertaken on a routine basis); and investigative monitoring (carried out where the reason of any exceedance for ecological and chemical status is unknown). Until now, no clear guidance exists for the investigative monitoring, as it must be tackled on a 'case-by-case' basis (BORJA et al. 2008b).

This contribution presents a methodology for:

- including sediments in the integrative assessment of the Ecological Status of the marine systems
- applying integrated sediment quality approaches in cases where investigative monitoring is needed

2 Methods

2.1 To integrate sediments to assess the Ecological Status

The methodology used is based in a long term (1995-2008) data set from an Environmental Monitoring Programme of transitional and coastal waters along the Basque Coast (Northern Spain). This Monitoring Programme comprises the analysis of both physico-chemical (in waters, sediments and biota) and biological elements (phytoplankton, macroalgae, benthos and fishes). The data set includes 19 stations in the coastal waters and 32 stations in estuaries, distributed in 18 water bodies (14 estuarine and 4 coastal) in 12 river catchments (Figure 1).

This network has been adapted to the requirements of the WFD since 2002 and hence, reference conditions were defined for different elements (BORJA et al. 2004b, BALD 2005) and pressures and impacts in transitional and coastal waters were identified (BORJA et al. 2006). The ecological status (bad, poor, moderate, good, high) is derived integrating the results of the quality assessment for physico-chemistry in waters (these are related mostly with eutrophic processes, such as nutrients, oxygen, etc. (BALD 2005, FERREIRA et al. 2007, LOUREIRO et al. 2006)) and biological elements (phytoplankton, fishes, benthos and macroalgae) (BORJA et al. 2004b). On the other hand, in the ES assessment the chemical elements play an important role and the chemical status is addressed. In the WFD the chemical status refers only to priority substances in waters and follows the "one out, all out" approach to assess the status; this means that the worst status of the elements (or priority substances) used in the assessment determines the final status (BORJA 2005, HEISKANEN et al. 2004).

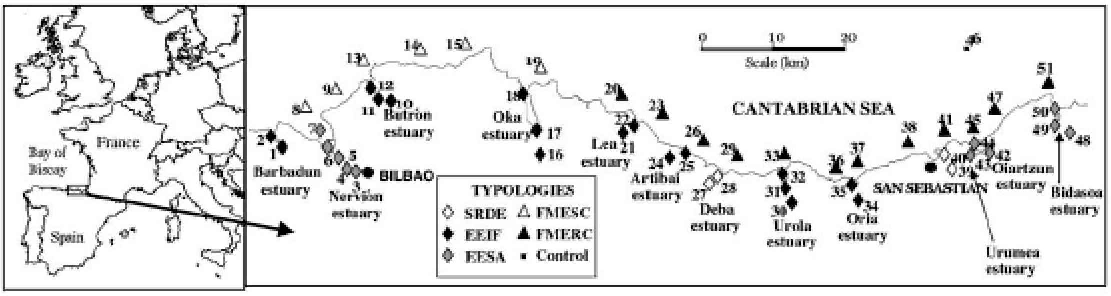

Figure 1: Sampling stations within the Environmental Monitoring Network of the Basque Country. Typologies: SRDE: Small river-dominated estuaries; EEIF: Estuaries with extensive intertidal flats; EESA: Estuaries with extensive subtidal areas; FMESC: Full marine exposed, sandy coast; FMERC: Full marine exposed, rocky coast (from BORJA et al. 2004a).

Our proposal is to integrate chemical elements in waters, sediments and biota for the chemical status assessment. The methodology used follows a decision-tree approach as is illustrated in figure 2 (BORJA et al. 2004a, 2008a).

WATER	SEDIMENT	BIOMONITORS	ASSESSMENT
All variables meet	All variables meet		Meet Chemical Status
	1 variable not meet		
	>=2 not meet		Not Meet Chemical Status
1 variable not meet	All variables meet		Meet Chemical Status
	1 variable not meet	All variables meet	
		No data	
		>=1 not meet	Not Meet Chemical Status
	>=2 not meet		
>=2 not meet			

Figure 2: Proposed scheme to integrate water, sediment and biota in establishing the chemical status.

This integration considers the responses of biological indicators and therefore is more realistic and discriminative than the "one out, all out" approach.
Quality objective levels for metals and organic compounds published in European and Spanish legislations for waters, sediments and biota have been used to assess the meet/do not meet chemical quality. Besides, Quality Objective Levels for metals in sediments have been developed and background levels are used in assessing high chemical status as is detailed in the scheme below (Figure 3, RODRÍGUEZ et al. 2006).

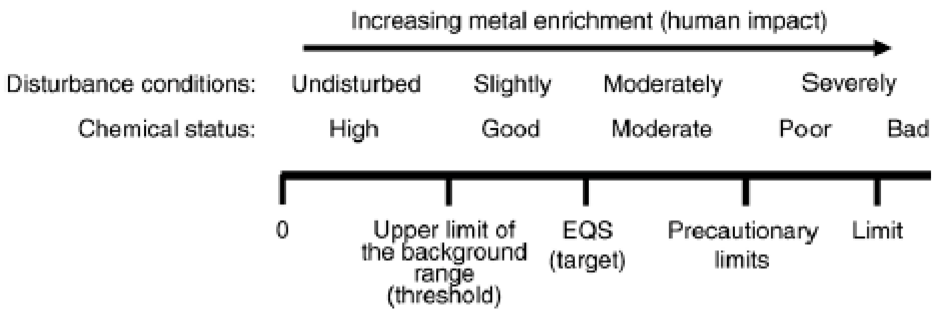

Figure 3: Relationships between increasing disturbance, due to metal contamination, and chemical status, according to the WFD and EMS terminology (from RODRÍGUEZ et al. 2006).

2.2 To apply integrated sediment quality approaches for implementing investigative monitoring studies

Only limited investigation has been made in relation to monitoring within the WFD. Some researchers have analyzed alternatives for monitoring transitional and coastal waters with the aim of fulfilling the main goal of the WFD: the achievement of good ecological status and its inherent assumption of the effective protection of the ecosystem structure and functioning (ALLAN et al. 2006, DE JONGE et al. 2006). The monitoring programmes can be of three types, as described below (from BORJA et al. 2008b).

(i) Surveillance monitoring, undertaken on routine basis for periodically evaluating the status of waters, and long-term changes.

(ii) Operational monitoring, in order to: establish the status of those bodies identified as being at risk of failing to meet their environmental objectives; and assess any changes in the status of such bodies resulting from the programmes of measures.

(iii) Investigative monitoring carried out: where the reason of any exceedance for ecological and chemical status is unknown; where surveillance monitoring indicates that the objectives for a water body are not likely to be achieved (and determine the causes); or to ascertain the magnitude and impacts of 'accidental' pollution.

To the knowledge of the authors, although the surveillance and operational monitoring networks should have been operative by December 2006, no European Member State has undertaken, until now, investigative monitoring within the WFD. Both surveillance and operational monitoring have some implementation guidelines in the WFD, in terms of the elements to be monitored, parameters, frequency, selection of sites, etc.; however, it is important to emphasise that investigative monitoring should be adapted to each particular case.

BORJA et al. (2008b) propose for investigative monitoring an integrated quality assessment approaches that combine several components (such as chemical analyses, acute toxicity assessments, and biological elements) providing an integrated view of the problem. The authors use the slag disposal from a blast furnace to a coastal area, as a case-study in implementing investigative monitoring, according to the WFD. This work consists on geophysical study to determine the extent of the disposal area; metal analysis in sediments; and an ecotoxicological study using Microtox test and an amphipods bioassay.

3 Results and discussion

The WFD and the European Marine Strategy define the chemical "High Status" when concentrations of specific pollutants remain within the range normally associated with undisturbed conditions. The studies undertaken along the Basque coast contribute to the assessment of regional undisturbed sediment conditions, based upon the methodologies which determine the metal background levels and the use of quality objectives levels in assessing chemical status. The authors propose the incorporation of sediments and biomonitors for determining the quality standards in the context of the WFD. The procedure presented here improves the final ecological quality determination as combine several parameters instead of using a simple index. Besides, it is more realistic and discriminative since considers the responses of biological indicators.

For implementing investigative monitoring within the WFD, the example presented here focuses upon a slag disposal (sediment quality problem) in the Basque coast that produces the risk of not achieving good status. By using the TRIAD approach that combines chemical analyses, acute toxicity assessments and biological parameters, an integrated view of the problem and a clear estimation of the potential risk associated with the slag disposal were obtained. In fact, slag dumping along the Basque coast, during most of the 20^{th} century, has not produced toxicological or harmful effects in the biota, some 12 years after the abandonment of the activity. It seems that the dispersion and dilution of the materials, the sediment and material composition, together with low bioavailability, do not generate an acute toxic effect (as detected by ecotoxicological tests); this does not represent a risk in achieving good ecological status, sensu WFD, by 2005 (BORJA et al. 2008).

4 Summary and conclusions

It is inferred that there are suitable tools for the assessment of the ecological status. The results obtained from integrative approaches are consistent with the knowledge and experience we have from our systems in the Basque coast. The principle 'one out, all out' is not real, and it must be discussed. It is more appropriate to combine several parameters than to use one simple index.

In the case of sediment quality assessment, the use of some methodological approaches, such as TRIAD or 'weight of evidence'(WOE) can assist in implementing investigative monitoring studies for polluted sediments, within the WFD.

The methodologies for ecosystem management must be based on science and on the expert judgment. But we have to keep in mind that complex methodologies are not suitable for management as we need to be practical and pragmatic. A balance between both needs must be found.

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Participation on Monitoring Networks along the Basque coast line

Participation on European and National Networks: SedNet and InterSed

Implementation of sediments (SEPM) in the WFD 2009

Mathias Ricking

Zusammenfassung

Die Probennahme von Sedimenten und Schwebstoffen bzw. schwebstoffbürtigen Sedimenten ist im Rahmen der Wasserrahmenrichtlinie der EU ein alternatives Kompartiment für das Monitoring der chemischen Gewässergüte sowie des Trends. Vor- und Nachteile einzelner Verfahren sind dargestellt. Eine prinzipielle Empfehlung kann nicht gegeben werden, im Einzelfall ist in Abstimmung mit den River-Basin-Management Plänen eine geeignete Strategie zu entwerfen.

Summary

The recommendations of the upcoming WFD Guideline for Sediment and Biota Monitoring are presented and initial experiences made within the ESB are presented. Advantages, disadvantages and remarks are illustrated. No general recommendation is given as the decisions are to be made on site-specific knowledge provided within the River-Basin-Management Plans.

1 Introduction

Within the Water Framework Directive (WFD) of the EU monitoring programmes are realised in the whole water phase (dissolved - < 0.45 µm - and particle associated). For monitoring the particle-associated and bioaccumulative contaminants the Chemical Monitoring Activity (CMA) got the mandate for 2007-2009 to propose a guideline for the chemical monitoring in sediments and biota (benthos organisms) to accomplish the WFD. The guideline will cover all freshwater ecosystems, the transitional waters and the open sea.

The sampling frequency is intended every 1-3 years for freshwater systems and up to 6 years for lakes and transition water bodies up to the open sea. During each sampling campaign the top 5-10 cm will be collected in net-accumulation areas to analyse the actual degree of contamination of the benthos habitat and to analyse for trends within representative water bodies at 3 or more sampling locations along every river section with 3 -5 composite samples each.

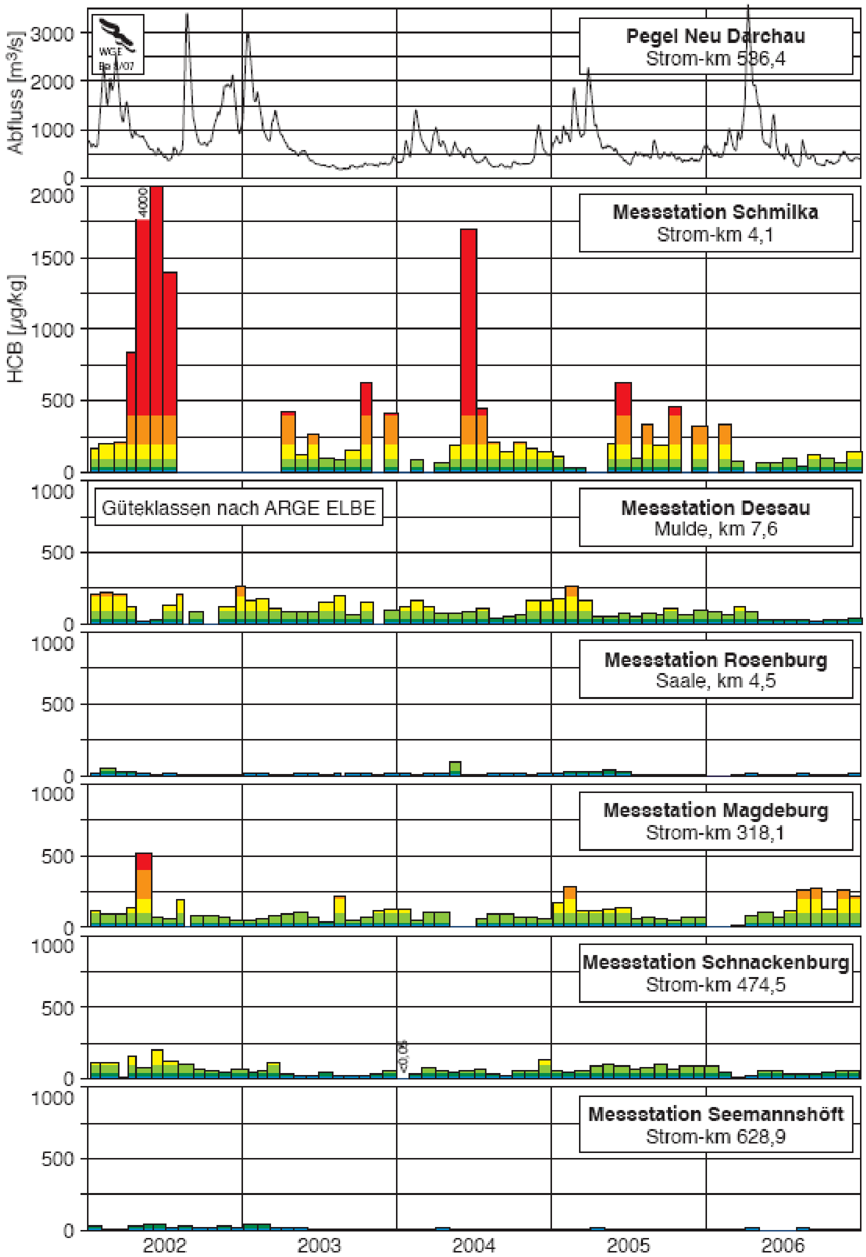

Figure 1: Seasonal variation of HCB in SEPM at different measuring stations along the Elbe River between 2002 – 2006 (Source: ARGE Elbe 2008). The upper paragraph shows the discharge [m³/s].

Additionally, sediment cores are to be collected to perform retrospective analyses back to the starting of the industrial activities. Sampling requirements, technologies and sample preparation are included in detail.

The actual discussion on sediment monitoring includes the opportunity to perform the monitoring alternatively on settling particulate matter (SEPM) by means of passive sampling devices or on suspended particulate matter (SPM) by means of flow-through centrifuges. The differentiation between SEPM and SPM is mainly for the transition zone and marine area where the dynamic exchange between sediment and SPM is incomplete if all. For the WFD water samples with more than 500 mg/L are considered to be treated in different ways (AMPS 2004).

Starting in 2002 the Environmental Specimen Bank of Germany (ESB) applies the recommendations included in the upcoming guideline since 2005 while starting the routine sampling campaigns.

The initial aim was to collect every 5-6 years surface sediments as depots for the particulate phase. Due to the highly variable particle concentration during the seasons and erosion via the flood event in summer 2002 on the Elbe River (see figure 1) and the almost complete failure to match the sediment accumulation between 2000 – 2005 during the sediment sampling campaign in 2005 the ESB shifted completely to the continuous sampling of SEPM by means of a sedimentation box (SB) for the river sampling sites. The SB are deployed in measuring stations and open water systems on landing stages, buoys. Experiences with different sampling technologies are presented and compared with the intended sampling strategy for sediments within the WFD.

2 Methods of sampling

The methods and sampling locations are published (SCHULZE et al. 2007), actual modifications on the sedimentation box and future developments will be addressed within this year. All passive sampling devices operate under gravity (1 g) like the systems used by the BfG (Bisam Sampler) or monitoring programs of the ICPE, ICPR (Sedimentation Basin) (DVWK 1999). In principle these devices reduce the flow velocity by means of blades and the SPM settles and accumulates. Compared to these devices flow-through centrifuges are used for freight calculations due to the fact that all suspended particulate matter including the ultra-fine material is collected. This system operates at 15000 – 24000 g.

The systems deliver comparable concentration data for most of the compounds in discrete grain-size fractions. Even flood events in 2005 and 2006 were included. The concentrations in surface sediments are fairly comparable to SEPM – samples (see figures 2 to 4).

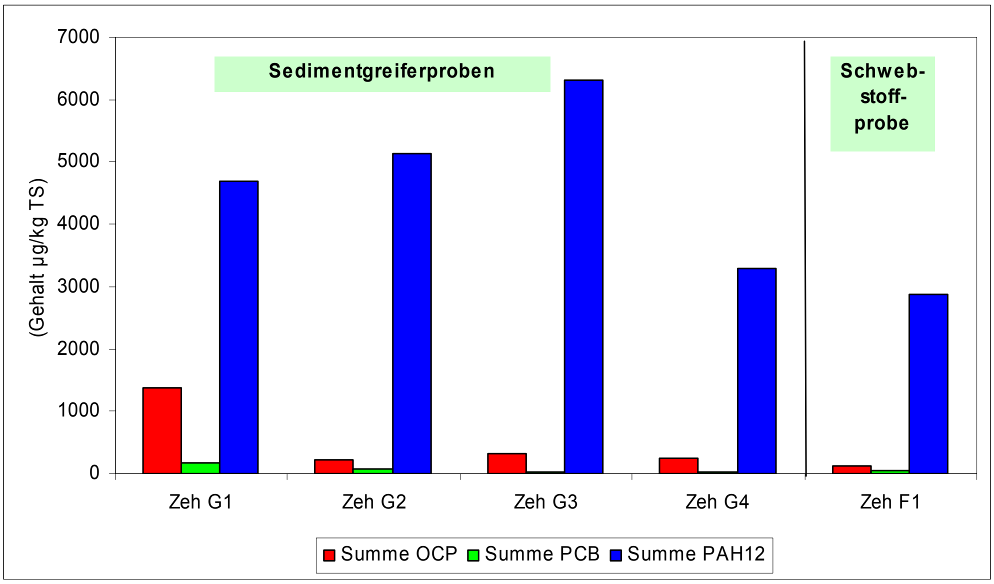

Figure 2: Sum of OCP, PCB and 12 EPA-PAH [ng/g d.m.] in grab (Zeh G1-G4) samples and a SB-sample (Zeh F1) at the sampling location Zehren (close to Meißen) on the Elbe River.

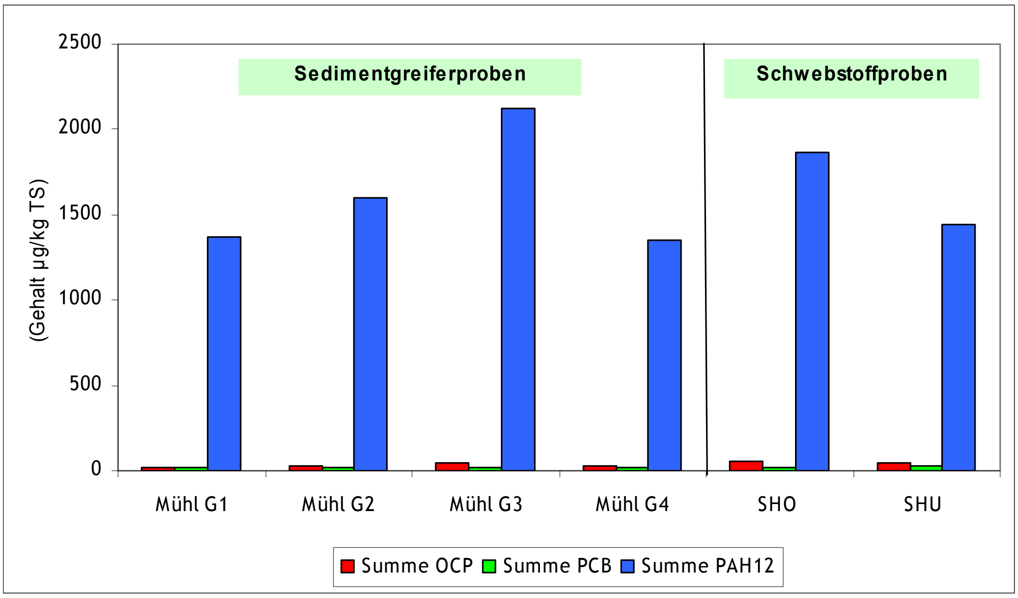

Figure 3: Sum of OCP, PCB and 12 EPA-PAH [ng/g d.m.] in grab (Mühl G1-G4) samples and two SB-sample (SHO and SHU) at the sampling location Blankenese and Mühlenberger Loch (Hamburg) on the Elbe River.

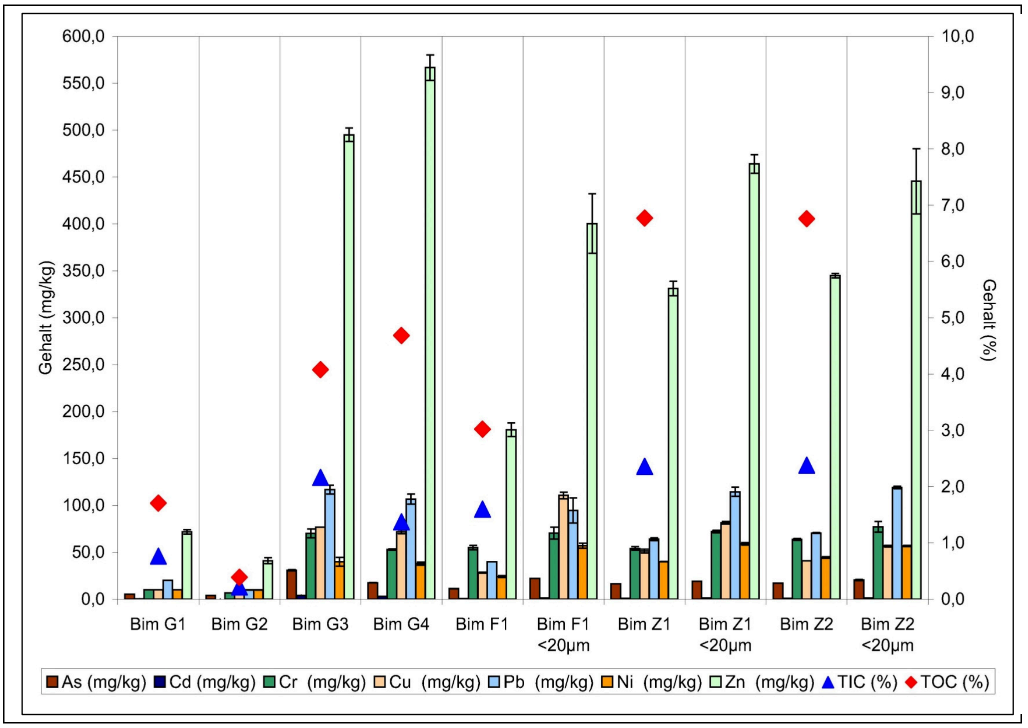

Figure 4: Elements [mg/kg d.m.] in grab samples (Bim G1-G4) compared to SEPM- and SPM-samples (Bim F1 and Bim Z1/2; Padberg Centrifuge Z61) at the sampling location Bimmen on the Rhine River.

In figure 4 the differences in collecting the ultra-fine fraction between the centrifuge and the SB are illustrated by the almost twofold difference in TOC between the sample Bim F1 and the samples Bim Z1 and Z2. Analysing the trace metal concentration in the < 20 µm or < 63 µm delivers the same concentrations (data for < 63 µm not shown).

The yearly homogenates of the SEPM samples collected by the ESB are in the same concentration range as published data by the ARGE Elbe (see table 1), as revealed by the initial analyses for the Mulde River (Dessau) for the compounds β-HCH and HCB (data: ESB unpublished).

Table 1
Variation of selected contaminants [ng/g d.m.] at the sampling location Dessau for 2005 and 2006 (data: ARGE Elbe).

	ß-HCH 2005	HCB 2005	ß-HCH 2006	HCB 2006
Minimum	6	48	61	22
Maximum	2900	270	1400	120
Average	620	100	310	50
Q25	140	57	79	26
Q75	740	160	460	84

The dating of the sediment cores taken in 2005 revealed for almost all sampling locations except 3 out of 13 disturbed sediments with sediment accumulation rates of more than 30 cm within days to weeks due to the 2002 Elbe flood (ESB unpublished). In some cases the sediment was inverted with older sediment layers on top.

The comparable data for the cases where no sediment is available (e. g. Mulde River in Dessau) or the sediment cores are mixed (like on most sampling locations of the ESB in 2005) lead to the promising substitution of the sediment sampling by SEPM-technologies. The yearly homogenates of the monthly taken samples reduce the analytical costs.

There is no method recommended for all situations, advantages and disadvantages are listed in table 2 and the decision is to be made based on the local knowledge according to the River Basin Management Plans. They have to address the question how actual is the 5 – 10 cm sample keeping in mind sedimentation rates of more than 1 m in estuarine areas like the Elbe, Scheldt or Ems River mouth.

Outlook

Due to the still limited efficiency in removing particulate matter by means of passive sampling devices, especially for the ultra fine light weight fraction, a small scientific cooperation project between the BfG and FUB for improvement of the removal effectiveness started this spring.

Table 2
Comparison of the different sampling strategies including advantages and disadvantages of each strategy.

Method	Advantage	Disadvantage	Remarks
Sediment coring	Low costs due to annual performance.	The net-sediment accumulation might not represent the exposure/ habitat for the whole year. Due to erosion and flood event accumulation the time trend analysis might be obscured.	The application of grab sampling devices is only recommended for situations with very controlled conditions. The collection by means of sediment coring systems is preferred especially when acrylic glass tubes are applied and the sediment is visually observed. In the case of deeper water bodies ships and heavy equipment increase the costs. In any way the sediment accumulation rate is highly recommended to be analysed.
SEPM (devices operating under 1 g gravity)	Low costs due to sampling intervals of 1-3 months or even longer.	The ultra fine light material is only partially collected.	The passive sampling technologies offer the opportunity for continuously sampling and yearly homogenates reduce the analytical costs.
SPM (devices operating under high gravity, e.g. 24000 g)	High efficiency in collection of all kinds of particulate material.	High costs (personal and equipment) and non-continuously sampling.	This technology is recommended for freight calculations as almost all particles are collected.

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Guideline for Monitoring of Sediments and Biota within the WFD (CMA-Group) (2008-2009)

Recommendations for sediment and suspended matter monitoring within the Elbe catchment area (2009)

Sediment quality assessment in the Netherlands: Linking science to policy

Piet J. den Besten

Zusammenfassung

Die Erkenntnis, dass die Verunreinigung von Sedimenten ernsthafte Gesundheitsgefährdungen beim Menschen und Bedrohungen der ökologischen Qualität unserer Gewässersysteme hervorrufen kann, führte in den späten 70er- und frühen 80er-Jahren in den Niederlanden und den Nachbarländern zur Umsetzung von Strategien, die auf die Vermeidung von (weiteren) Gewässerverunreinigungen und zur Sanierung (bzw. oft auch Beseitigung) von stark verunreinigten Sedimenten abzielten. Neben einem nationalen Strategiedokument zur Gewässerbewirtschaftung (Gesetz über die Verschmutzung von Oberflächengewässern, 1970), enthält auch das Bodenschutzgesetz (ursprünglich aus dem Jahr 1987) seit 1997 einen Abschnitt, der sich mit verunreinigtem Sediment befasst. Dieses Gesetz stellt Qualitätsziele und Grenzwerte für Schadstoffgehalte in Böden und Sedimenten auf, bei deren Überschreitung Sanierungsmaßnahmen in Betracht zu ziehen sind. Ein weiterer Abschnitt (eine Durchführungsbestimmung zum Abschnitt "Vermeidung" in diesem Gesetz; allerdings ebenso mit Bezug zum Gesetz über die Verschmutzung von Oberflächengewässern) ist die Verordnung über Baumaterialien, die teilweise entwickelt wurde, um die nutzvolle Verwendung von Baggergut zu regeln. Letztere wurde 2008 durch den Erlass zur Bodenqualität ersetzt, der die Folge neuer strategischer Zielsetzungen hinsichtlich des Risikomanagements und der Schaffung von Möglichkeiten für die Wiederverwendung von Bodenmaterial und Sedimenten (Baggergut) je nach dem Grad der Verunreinigung darstellt (Ministry of Housing, Spatial Planning and the Environment 2007).

Introduction

Awareness that sediment pollution can pose serious threads to human health and ecological quality of our water systems led in the late 70ies / early 80ies in The Netherlands and neighboring countries to the implementation of policies aiming at the prevention of (further) water pollution and at the remediation (often removal) of sediments that had become severely contaminated. Apart from a national policy document on water-management (act on surface water pollution, 1970), the soil protection act (originating from 1987) contains since 1997 also a part dealing with contaminated sediment. This act provides quality objectives and intervention values for contaminant levels in soils and sediments above which remediation should be considered. Another part (an ordinance to the prevention section of this act (but also linked to the surface water pollution act) is the Building Material Decree, part of which was developed to regulate the beneficial reuse of dredged material. The latter part has in 2008 been replaced by the Soil Quality Decree, which is the consequence of new policy objectives with regard to risk management and creating re-use possibilities of soil and sediment (dredged material), depending on the degree of contamination (Ministry of Housing, Spatial Planning and the Environment 2007).

Sediment quality assessment

In general, two main goals for sediment and dredged material assessment procedures can be distinguished:

(i) assessment of the *in-situ* quality of sediments and resulting risks at sites where sediment remediation is to be considered, and

(ii) assessment of the *ex-situ* quality of dredged sediments in order to select dredged material relocation and sediment management options for maintenance and capital dredging on the one hand (e. g., free and confined disposal or treatment options) and on the other hand for the evaluation of environmental impacts of projected new-construction work.

Assessment of the *in-situ* quality of sediment

For freshwater systems in The Netherlands, assessment of *in-situ* sediment quality is required within the legal framework of the Soil Protection Act (Ministry of Housing, Spatial Planning and the Environment 1994). This act requires tiered risk assessment as a second tier for sediments with contaminant concentrations above the intervention value, in order to determine the urgency of remedial action[1]. In order to evaluate human risks, model calculations are carried out in order to quantify the extent to which humans (adults/children) can be exposed to contaminant via food consumption or via recreation activities in water. When the exposure exceeds maximum permissible risk criteria, actual risk is concluded. The model is based on general assumptions with regard to behaviour and diet of human populations. Investigation of the risk for transport of contaminants from the sediment to groundwater, or to surface water. Model calculations are carried out in order to quantify the extent to which these processes occur. When contaminant fluxes (preferably calculated from field data) exceed high risk criteria, actual risk is concluded. Ecological risks are evaluated using the Triad approach[2].
In the Dutch version of the TRIAD, bioaccumulation measurements are also considered,

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[1] In 2009 the Water Act will become into force, after which sediment risk assessment will be carried out in relation to water management (WFD) objectives instead of the objectives of the soil protection act.

[2] At this moment, first a msPAF calculation is carried out before a Triad assessment is carried out, as a first step the potentially affected fraction of species (msPAF; POSTHUMA et al. 2002) will be calculated using the model OMEGA. The msPAF is used as indicator of the toxic pressure in the sediment (more information is given below).

using the results of laboratory tests, or preferably by measurements in indigenous organisms (DEN BESTEN et al. 1995). Based on the most sensitive parameter, sediments are classified for the categories "field observations" and "bioassays" as either "-" (no effect/risk), "±" (moderate effect/risk) or "+" (strong effect/high risk). The goal is to elucidate the relationship between effects on macrozoobenthos and responses of bioassays which, in turn, can be related to levels of chemical pollution. For that purpose, chemical concentrations are converted into “toxic units” (TU): these are the ratio between the chemical’s normalized concentration and the lowest NOEC reported in the literature, among the bioassays included in the battery (DEN BESTEN 1995). High risk is inferred when strong effects are observed in field surveys and/or bioassays that can be related to chemicals present in the sediment (see VAN ELSWIJK et al. 2001).

In The Netherlands, the Triad has been carried out routinely using the following bioassays:

> *Chironomus riparius* (test with midge larvae in whole sediment samples)
> *Daphnia magna* (water flea; test with sediment pore water)
> *Photobacterium phosphoreum* (also known as Microtox assay; sediment pore water)

In addition, three other bioassays have been applied in a small number of studies:

> *Thamnocephalus platyurus* (sediment pore water bioassay with a freshwater crustacean)
> *Brachionus calyciflorus* (sediment pore water bioassay with rotifers)
> *Ephoron virgo* (test with mayfly larvae)

The risks of food-chain poisoning as a result of bioaccumulation can be assessed in two ways (VAN ELSWIJK et al. 2001):

> By collecting organisms from the field. In The Netherlands bioaccumulation has been measured as part of studies on the risks caused by sediment pollution. Contaminant levels have been measured in chironomids, oligochaetes, fish and Cormorant eggs (DEN BESTEN et al. 1995). The contaminant levels were evaluated by comparison with threshold values for foodchain poisoning (maximum permissible risk concentrations - MPCs) that have derived specifically for a number of food sources for predators of aquatic ecosystems (DEN BESTEN et al. 1995).

> By performing the accumulation bioassays with aquatic worms according to the method described by MAAS et al. (1993) and DEN BESTEN (2003). Aquatic worms are exposed for 4 weeks to samples of sediment in the laboratory after which the organisms are collected and processed for analyses of the contaminant levels. Accumulation is evaluated by comparing the accumulation levels with reference values and with threshold values for foodchain poisoning (MPCs).

Case studies

As explained above, the Triad approach has been used in The Netherlands for the selection of remediation sites. Remediation projects have been carried that resulted in significant improvement of the ecological quality of the water system as a whole. Examples are the pilot remediation of a site in the Nieuwe Merwede (see below) and the remediation of the river

Hollandsche IJssel, where severely polluted sediments in the banks of the river have been capped (and partly removed) in combination with nature restoration afterwards. However, there are also situations where the net-effect of sediment remediation will be small. This can be the case because upstream contaminant sources have not yet been regulated. For example, the poor quality of sediments in the river Meuse was shown to lead to recontamination of remediated sites which corresponded with only a temporal reduction in sediment toxicity (DEN BESTEN & VAN DEN BRINK 2005). The situation is different in parts of the delta that are influenced (only) by the river Rhine. In a pilot remediation of a site in the Nieuwe Merwede, sediment quality improved significantly after remediation (DEN BESTEN & VAN DEN BRINK 2005). However, because in the past decades water quality of the river Rhine has improved, the quality of fresh sediment entering the delta from upstream parts of this river also has shown a significant improvement. This was also observed in the response of bioassays with sediment or sediment pore water. Therefore, if in polluted sites natural capping with this material does occur, then from the point of view of ecological risks, remediation has no net positive effect. Therefore, sites with high ecological risk because of sediment contamination and with a low input of fresh sediment should be given highest priority (DEN BESTEN & VAN DEN BRINK 2005). In a broader perspective this underlines the frequently obtained conclusion that for effective sediment management, a proper understanding of sediment dynamics on the water system scale is required.

Recent changes in the risk assessment framework

With the implementation of the new Water Act (starting in 2009) a new framework for sediment quality assessment will be used that is more in line with monitoring for the WFD. Sediment remediation is regarded as one of the possible measures that can help to realize WFD objectives (if remediation is not triggered by high risks for human health or for ground water contamination). From the point of view of WFD requirements, the ecological indicators of water (and sediment quality) will become an important trigger for further research. The Triad components described above will be used in a different way. On the basis of ecological quality ratio (EQR) values that are related to the benthic community, sediments can be identified as possible limiting factor for WFD objectives. Before bioassays are used to confirm this, as a first step the potentially affected fraction of species (msPAF; POSTHUMA et al. 2002) will be calculated, as indicator of the toxic pressure in the sediment. This calculation is carried out using the model OMEGA, and with bioavailable concentrations of contaminants in the sediment as the model input. The methodology for calculating a msPAF value has also been developed for the assessment of risks of soil contamination (MESMAN et al. 2003). With this model, direct effects and effects as a result of foodchain poisoning can be distinguished. In The Netherlands, mild extraction techniques with $CaCl_2$ or Tenax are used for measurement of the contaminant concentrations considered to be bioavailable (CORNELISSEN et al. 2001; see also VAN ELSWIJK et al. 2001). Bioassays are optional as instruments in a next Tier, to complete a line of evidence according to the original Triad concept. It is expected that the described framework for sediment quality assessment will also be linked to other policy objectives such as in the habitat directive/nature 2000 legislation and the directive on food quality (the latter for fisheries or agriculture).

Assessment of the *ex-situ* quality of sediment

The Chemistry-Toxicity Test (CTT) was developed for the assessment of the quality of dredged material and the decision for free disposal of the material in the North Sea. For the CTT three bioassays were selected for routine application: a test the mud shrimp *Corophium volutator*; the bacterial test Microtox Solid Phase and a test with a genetically modified cell line that reacts specifically to substances with a dioxin-like mode of action (DR-CALUX). The reason for including bioassays was that they would help to detect a larger group of contaminants, with relevance for the protection of the marine ecosystem (SCHIPPER 2004). However, recently it was decided not to implement these test for a number of reasons:

> Lack of a representative dataset showing the discriminative power of the bioassays;
> Sediments have become less toxic over the past decades.
> Lack of a good basis for quality assurance/quality control for the bioassays;
> Together with changed priorities in water management (more attention to monitor and reduce contaminant sources than *end of pipe* measures).

Recent developments in ecotoxicology in The Netherlands

> *In-situ* bioassays have over the past decade gained increased attention and acceptance as ways to improve the ability to link cause and effect in aquatic ecotoxicological studies. One of the main advantages provided by *in-situ* tests compared to more conventional approaches is better control over “stressor” exposure to a defined population of test animals under natural or near-natural field conditions. By partly controlling what environmental compartment(s) a known or standardized number of test animals are in contact with, the researcher can have an improved ability to describe and link cause and effect. In short, when conducted properly, *in-situ* tests can provide improved diagnostic ability and high ecological relevance. *In-situ* approaches also allow for some level of “control” and replication within natural systems. For example, in translocation experiments with the field bioassays with *C. riparius*, the influence of surface water quality on the benthic community was demonstrated. Clean sediment was placed in a polluted site, and vice versa. Field bioassays performed during the winter season indicate that low temperatures can interact with or add to the effects of sediment contamination on chironomid populations (DEN BESTEN et al. 2003).

> For assessment of sediment quality with bioassays it is important that the assay is able to mimic natural conditions. A new technique was developed that meets this requirement, leaving sample and geochemical conditions intact. Exposure tests were conducted with two aquatic species that occur in sediment and water, respectively. Comparison between the two methods showed that the standard protocol tends to overestimate risks for PAHs, and underestimates the risks for heavy metals, in terms of accumulated amounts. Sample handling largely affected chemical speciation, and exposure concentrations deviated from the ones observed in the undisturbed setting. This new approach may contribute to better-founded quality criteria for sediments or improved testing protocols for sediment bioassays (VINK et al. 2005).

> Effect-Directed Analysis (EDA). EDA is a promising tool for the identification of organic toxicants in complex mixtures. EDA aims at the identification of chemical causes of toxic effects (see also below, **Opportunities for further development of bioassays**).

> There is growing criticism on the use of animals in toxicity tests. This has lead to an enhanced attention for alternative test systems, with plants or bacteria as test species, or with immortalized cell lines derived from animals. With regard to the detection of chemicals, these in vitro bioassays may either be “broad spectrum” or so called "toxic mechanism based" assays. Examples of the first type of bioassays are the Microtox assay and biochemical endpoints in fish cell lines. Examples of toxic mechanism based assays are the Mutatox and Umu-C (genotoxicity), DR-CALUX (dioxin-like or Ah-mediated toxicity), ER-CALUX (estrogenic toxicity) and AR-CALUX (androgenic toxicity). In The Netherlands and elsewhere, cytoxicity measurements with fish cell lines have been studied for their value as a screening parameters for the detection of effluent toxicity BABICH & BORENFREUND 1991; GAGNÉ & BLAISE 1997; TUK & DEN BESTEN 2001). Apart from broad spectrum endpoints such as crystal violett, MTT and neutral red uptake, also markers for genotoxicity have been used in fish cell lines (HOLLERT et al. 2000; NEHLS & SEGNER 2001). In The Netherlands, the *in-vitro* bioassay with the fish cell line RTG-2 has been used in the BECPELAG project (DEN BESTEN et al. 2006).

Towards EU Sediment quality standards?

In The Netherlands, sediment quality standards (SQSs) are used within the framework of the Soil Quality Decree, for the evaluation of relocation and re-use possibilities of soil and sediment (see **Introduction**). Application of SQSs for the evaluation of sediment remediation measures has been done in tiered approaches, where the SQSs are only used as trigger values (see the section on the **Assessment of the *in-situ* quality of sediment**).

In 2002, the pro’s and contra’s for the application of SQSs were evaluated in a Pellston workshop (WENNING 2005). Concerns about the use of SQSs reported from this workshop are for instance:

> the ability to adequately predict the presence of absence of chronic toxicity to sediment-dwelling organisms under field conditions;

> the ability of SQSs to predict effects caused by accumulation in foodchains;

> doubts whether SQSs can be used to demonstrate cause-effect relationships;

> concern whether SQSs based on particular endpoints can be used to predict other toxicity endpoints and mechanisms.

Application of SQSs as trigger values (in tiered approaches) is a way of getting around these uncertainties, which has been advised by several expert groups.

The EU Water Framework Directive (WFD) Expert Group on Analysis and Monitoring of Priority Substances (AMPS) drafted in 2004 a discussion document on sediment monitoring. According to the drafting group, the aim of sediment monitoring under the WFD is: 1) to establish the criteria for, and to provide a demonstration of, conditions of “no deterioration” in sediment quality; 2) to provide data on sediment quality across the EU; 3) to monitor the progressive reduction in contaminants and phasing out of Priority Hazardous Substances (PHS) based on a statistically robust sampling strategy (trend monitoring: temporal & geographical). Compliance monitoring is not yet appropriate because of the lack of a definition of valid Environmental Quality Standards (EQS sediment) in a European context (and the complexity of the task of producing one), analytical limitations and the anticipated costs of obtaining full spatial coverage.

Opportunities for further development of bioassays

Today the European Water Framework Directive provides the basis for transnational EU water legislation. Under the WFD, the focus on contaminated sediments will change considerably due to the holistic approach integrated in the framework directive and the subsequent need for an improved understanding of the ecological and ecotoxicological impact of sediments and dredged material on the aquatic environmental quality. When in a given water system the chemical and ecological objectives (defined as a good ecological status) are not met, specific measures need to be included in the river basin management plan. While the focus is on water quality and therefore on the management of (upstream) pollution sources, one of the possible measures is sediment remediation. In order to evaluate whether sediment remediation would be an effective measure for the improvement of the chemical and ecological status, risk assessment is required with special attention to the relation between sediment and water quality.

In waters where WFD objectives can not be met, there will be a need for diagnostic studies, in which also the role of contaminated sediments is to be evaluated (e. g., to distinguish toxic pressure by sediment contamination from other stress factors like eutrophication, habitat destruction etc.). In The Netherlands, the sediment quality assessment that so far has been part of the legal framework of the soil protection act, now is restructured in order to prioritise sediment remediation locations from the ‘WFD perspective’. This means that the main question of the risk assessment will shift from “Are there unacceptable risks for the ecosystem?” to “Is sediment quality the main limiting factor for reaching ecological objectives?”. One of the main benefits of the WFD and its monitoring programme is the use of both chemical and ecological parameters. The interpretation biological and chemical data could be improved by the use of two categories of bioassays, as proposed by VAN DEN HEUVEL et al. (2005):

1. Eco-assays: the use of tests as a tool to determine the causes of below-standard ecological status of water bodies. Eco-assays can be used as part of a diagnostic system to identify or confirm chemical, ecological or hydro-morphological pressures.
2. Bio-analysis: the use of bioassays to partially replace chemical analyses of priority pollutants or other relevant compounds in chemical monitoring. The goal is not an extended analysis of water quality, but a better indication of hazard (see also decription under the title “effect-directed analysis” given above).

Eco-assay is a collective term for a package of biological tests used to identify the causes of bad ecological status, whether they be chemical, hydromorphological or ecological. In any attempt to raise the ecological status of water systems ecoassays are needed to ensure that cause and effect are properly understood. The WFD system therefore offers a great deal of potential for the use of ecoassays, provided the various instruments are used correctly. Many biomarkers and bioassays are already used this way, and based on the experience with the Triad approach, a new concept for diagnostic purposes is within reach.

Perhaps the most challenging opportunity the WFD offers is the development and implementation of bio-analysis. In the near future, it should be possible to apply screening bioassays to select water or sediment samples for extensive chemical analysis. A step further could be that bioassays partially replace chemical analyses of priority pollutants or other relevant compounds in chemical monitoring. This could become the answer to the discussion about the thousands of chemicals present in the environment and impossible to analyse all. Effect-directed chemical characterization is expected to become a powerful and cost-effective approach when the mixture of chemicals is unknown. The development of simple and sensitive tests that allow for a high throughput capacity is a very promising research field and already receives a lot of attention by stakeholders (regulatory organisations, drinkwater companies etc.) (DEN BESTEN & MUNAWAR 2005). This is already the case for whole effluent toxicity assessment, but in the future screening bioassays may also be applied to obtain a first indication of the risks for the ecosystem.

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The SEDIMARD83 protocol proposed to assess the hazards linked to marine dredged sediments meant for land disposal, and illustration of the effects of various ageing protocols on the ecotoxicity and trace elements contents of fresh-water sediments

Christophe Mouvet and Christine Bazin

Zusammenfassung

In Frankreich müssen gebaggerte Sedimente bei Überschreitung bestimmter Schwermetall- und PCB-Konzentrationen an Land untergebracht und als Abfall angesehen werden, dessen Gefährlichkeit bzw. Unbedenklichkeit eingeschätzt werden muss. Die ökotoxische Charakterisierung des Abfalls ist der ausschlaggebende Unterscheidungsfaktor. Allerdings gibt es in Frankreich für solche Untersuchungen kein standardisiertes Verfahren. Die Unterbringung von Sedimenten an Land wirft auch die Frage auf, wie die Lagerung unter aeroben Bedingungen und ohne Wassersättigung die Ökoktoxizität der Sedimente und die Mobilität der darin enthaltenen Spurenmetalle beeinflusst.

Im Rahmen des französischen SEDIMARD83 Projekts wurde ein Verfahren auf der Grundlage von Biotesten zur Bewertung des Gefährdungspotenzials mariner Sedimente, die für die Unterbringung an Land vorgesehen sind, entwickelt und mit zehn Sedimenten aus verschiedenen Hafentypen getestet. Da das saline Porenwasser für *V. fisheri* und *D. magna* keinerlei Toxizität zeigt, kann es entfernt werden, ohne die Ökotoxizität des Sediments unterzubewerten. Das Sediment kann dann mit nicht-marinen Biotesten geprüft werden, die im Hinblick auf die Unterbringung an Land relevant sind. In einer Testbatterie von fünf limnischen und terrestrischen Biotesten erwiesen sich der chronische *Brachionus calicyflorus*-Test und die akuten terrestrischen *Avena sativa*- und *Brassica napus*-Pflanzenteste als die empfindlichsten. Eine Handlungsanweisung basierend auf diesen drei Testen und den dazugehörigen Schwellenwerten ermöglicht es herauszufinden, welches der zehn Sedimente ein ökotoxisches Potenzial aufweist und an Land als Sondermüll zu behandeln ist.

Im Rahmen der von S. Piou am französischen Forschungsinstitut CNRSSP und der Universität Metz durchgeführten Doktorarbeit wurden die Auswirkungen der Alterung von an Land abgelagerten Sedimente untersucht. Eine Laborstudie wurde mit stark schwermetallhaltigen

Süßwassersedimenten durchgeführt, bei denen der Alterungsprozesss mit drei verschiedenen Verfahren nachgebildet wurde. Aufeinanderfolgende Trocknungs- und Wiedervernässungszyklen unter aeroben Bedingungen führten zur signifikanten Erhöhung der Ökotoxizität für *Pseudokirchneriella subcapitata*.

Der Notwendigkeit der schnellen Reaktion auf das Gefahrenpotenzial gebaggerter Sedimente steht die Dauer der natürlichen Alterungsprozesse gegenüber. Deshalb wurden im BRGM chemische Behandlungsmethoden auf der Grundlage von Wasserstoffperoxid erprobt, um eine stark beschleunigte Oxidation zweier Süßwassersedimente zu stimulieren. Die bisherigen Ergebnisse sind vielversprechend, jedoch sind weitere Versuche nötig.

Abstract

Above certain concentrations in heavy metals and PCBs, sediments dredged in France must be disposed of on land and are then considered as wastes which hazardous or non hazardous character must be assessed. The ecotoxic character of the waste is a key discriminating factor for which no standardized protocol exists in France. The land disposal of sediments also raises the question of how the ageing in aerobic, non water-saturated conditions influences the ecotoxicity of the sediments and the mobility of the trace metals they contain.

In the framework of the French SEDIMARD83 project, a bioassay-based protocol to asses the hazardous character of marine sediments meant for land disposal has been developed and tested with 10 sediments from various harbour types. Since the salted pore water did not show any toxicity to *V. fisheri* and *D. magna*, it can be removed without underestimating the ecotoxicity of the sediment. The sediment can then be tested with non-marine bioassays relevant in view of land disposal. Amongst a battery of 5 freshwater and terrestrial bioassays, the most sensitive proved to be the chronic *Brachionus calicyflorus* test and the acute terrestrial *Avena sativa* and *Brassica napus* plant tests. An operational protocol based on these 3 tests and associated threshold values enables to identify which of the 10 sediments has an ecotoxic character and should be treated on land as hazardous waste.

As part of the PhD of S. Piou conducted in the French research Institute CNRSSP and the University of Metz, the effects of sediment ageing once disposed of on land have been investigated. A laboratory study was conducted with a freshwater sediment highly contaminated by trace metals and submitted to 3 protocols simulating ageing. Successive cycles of drying/rewetting in aerobic conditions lead to a significant increase in the ecotoxicity to *Pseudokirchneriella subcapitata*.

The need for rapid response on the hazardous character of dredged sediments is not compatible with the duration of natural ageing. Chemical treatments based on hydrogen peroxide have therefore been tested at BRGM to simulate a much accelerated oxidation of two freshwater sediments. The preliminary results are promising but further testings are required.

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since 2008:	Hazards linked to dredged sediments

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The ICPR sediment management plan for contaminated sediments

Martin Keller

Zusammenfassung

Eine Expertenarbeitsgruppe hat von der Internationalen Kommission zum Schutz des Rheins (IKSR) das Mandat bekommen, eine Gesamtstrategie für das Sedimentmanagement am Rheinstrom und den großen Nebenflüssen auszuarbeiten. Das Hauptziel ist dabei das Management von kontaminierten Sedimenten. Der Managementplan wird als Empfehlung an die verantwortlichen Behörden für die Erfüllung des Rheinübereinkommens gemäß Artikel 3, zur „Verbesserung der Sedimentqualität für die schadlose Verbringung von Baggergut", sowie für die Aufstellung der Maßnahmenprogramme in die WRRL-Bearbeitungsgebiete weitergegeben. Das Mandat umfasst drei Aufgaben: zunächst die Bestandsaufnahme kontaminierter Sedimente unter Einbeziehung bisheriger relevanter Sedimentstudien. Dies beinhaltet die Erfassung von Menge und Qualität der mit Schadstoffen belasteten Sedimente, die Bewertung und Klassifizierung der Sedimente gemäß ihrem Gefährdungspotenzial sowie Vorschläge für einen ökonomisch und ökologisch vertretbaren Umgang mit den Sedimenten der verschiedenen Sedimentklassen. Als zweite Aufgabe sollen die nationalen Vorschriften sowie internationale Empfehlungen und Handlungsstrategien zum Sediment- und Baggergutmanagement, die bisher im Rheingebiet angewandt wurden, in dem Gesamtkonzept angemessen berücksichtigt werden. Zum Dritten soll eine Übersicht über die Risikogebiete einschließlich der Prioritäten der Behandlung vorgelegt werden.

Für die Ausarbeitung des Sedimentmanagementplans waren die Ergebnisse des IKSR-Forschungsprojektes „Untersuchungen zum Resuspensionsrisiko von Sedimentablagerungen in ausgewählten Staustufen des Rheingebietes" aus den Jahren 2000-2003 wichtig. Die Untersuchungen kontaminierter Sedimentbereiche ergaben einen Schwerpunkt in bestimmten Staustufen des Oberrheins, die durch eine historische über viele Jahre andauernde Einleitung von Hexachlorbenzol (HCB) verunreinigt sind. Speziell Sedimentbereiche im Oberwasser der Staustufen Marckolsheim und Rhinau sind stark mit HCB verunreinigt und damit heute eine Quelle für Kontamination der Sedimente weiter flussabwärts.

Das Konzept für den Sedimentmanagementplan Rhein basiert wesentlich auf den Empfehlungen des Europäischen Sedimentnetzwerkes SedNet. Das Konzept beinhaltet eine regelbasierte Bewertung mit folgenden drei Schritten:

- Identifizierung und Klassifizierung der relevanten Schadstoffe im Rheingebiet
- Identifizierung und Klassifizierung der Gebiete mit relevanten verunreinigten Sedimentmengen
- Identifizierung und Klassifizierung der Risikogebiete

Die relevanten Schadstoffe sind sechs Schwermetalle und organische Schadstoffe wie PAK, HCB und PCB. Für den Grad der Verunreinigung wurde eine 5-stufige Klassifizierung auf der Basis der IKSR-Zielvorgaben gewählt. Das Remobilisierungsrisiko von verunreinigten Sedimenten wird anhand von Ergebnissen aus adäquaten Hochwasseruntersuchen abgeschätzt oder durch Vergleich der kritischen Sohlschubspannung der Sedimente mit den Sohlschubspannungen, die bei einem Hochwasser der Jährlichkeit 10 auftreten können. Von den insgesamt untersuchten 93 Sedimentbereichen wurden 22 als Risikogebiete identifiziert und weitere 18 als Gebiete, die einer besonderen Aufmerksamkeit bedürfen („areas of concern"). Für die hoch belasteten Sedimentbereiche in den Stauhaltungen von Marckolsheim und Rhinau wird empfohlen, eine Sanierung vorzusehen, weil diese Bereiche heute eine Quelle für die HCB-Kontamination der Sedimente flussabwärts darstellen.

1 Introduction

Since two years an ICPR expert group elaborates a comprehensive strategy for sediment management in the Rhine basin. Main objectives are a sediment management plan for contaminated sediments addressed to competent authorities in the watersheds for implementation in measure programmes according to WFD and the "improvement of sediment quality in order to relocate dredged material without harm" (Art. 3 of the ICPR Rhine Convention). The group consists of experts from the countries CH, D, F and NL. Water management authorities, waterways and shipping directorates, environment ministries and scientific institutes are involved.

In the last ten years a lot of sediment investigation had bee made to evaluate the level of contamination with heavy metals and organic micropollutants. A first inventory of contaminated sediment in the Rhine basin was published by HEISE (HEISE et al. 2004). On behalf of the International Commission for the Protection of the River Rhine (ICPR) in the years 2000 until 2003 a research project was carried out aiming at the level of resuspension risk of contaminated sediments (WITT et al. 2003, WITT 2004). In the following chapter the main results from impounded sections of the Upper Rhine are presented. The results of this ICPR research project have been an important part of the current draft of the comprehensive strategy for sediment management in the Rhine basin.

In chapter 4 the conceptual approach and results of the sediment management plan are discussed.

2 Investigations on resuspension risk of polluted sediments in the river Rhine and its tributaries

The main objective of the investigation was to obtain an insight into the erosion stability of contaminated sediment layers as a function of physical sediment parameters and to quantify the contamination. A risk remobilisation assessment based on both hydrodynamic and chemical parameters is thus developed for high water. At the Institute for Hydraulics, University of Stuttgart, a specific cohesive sediment erosion testing device has been developed to quantify the critical erosion shear stress. Further development of the experimental set-up enables to quantify not only the critical erosion shear stress but also the erosion rate as another key parameter in quantifying and modelling erosion processes. A special sediment sampling technique allowing undisturbed sampling of sediment cores with a diameter of 13,5 cm. An empirical correlation between the different physical parameters such as erodibility, bulk density, gas content etc. and chemical parameters can be established by parallel sampling of neighbouring sediment cores. These data allow to investigate different flood scenarios to provide a first estimate of the amount of released contaminants due to resuspension.

Due to chemical analyses the main relevant pollutant of the sediment cores in the Upper Rhine barrages is hexachlorobenzene (HCB). Sediments of the Lower Rhine and the Dutch Rhine are – in contrary – mainly contaminated with PCB and heavy metals like cadmium and mercury. In the tributary Main at the Eddersheim barrage high concentrations of cadmium, mercury, copper, lead, zink and also PCB could be found in the headwater sediments. But these Main sediments are partly consolidated and the risk of resuspension during high flood events is low.

The HCB contaminated sediments at the Upper Rhine barrages had shown low values of critical shear stress and therefore could easily be resuspended. For example the HCB release at the Marckolsheim barrage is estimated at 6 to 17 kg during high water (> 3000 m³/s). It is known that during the period 1960-1985 large amounts of HCB, mainly as by-product from chemical production near Rheinfelden (km 148) were discharged into the Upper Rhine. The contaminated sediments are moving downstream when they become remobilized (e. g. by high floods or dredging activities) and settle in areas of low flow velocity like the two final barrages in Gambsheim and Iffezheim. Table 1 shows HCB content of sediments in a depth of 0-1,2 m. The results are taken from the ICPR research project. Further investigations prove, that especially in the headwaters of the Marckolsheim and Rhinau barrages sediment contamination is a source for ongoing pollution downstream.

Table 1
Hexachlorobenzene concentrations of sediments in barrages of the Upper Rhine

Barrage	Average Value in µg/kg	Maximum Value in µg/kg
Iffezheim	158	910
Gambsheim	128	400
Strasbourg	223	2300
Gerstheim	135	1500
Marckolsheim	609	4100

3 The ICPR sediment initiative

The question is, a) how historic polluted sediments nowadays are of effect on the water and suspended sediment quality during high flood events and/or during dredging and relocation activities and b) are polluted sediments of the Upper Rhine also a risk for sediment quality in regions far downstream like the Netherlands? In 2005 the ICPR had given the mandate to the international expert group SEDI to answer these questions and to draft a sediment management plan for contaminated Rhine sediments. This included an inventory of relevant sediment studies so far, the determination of the extent of pollution and the quantity of polluted sediments, the assessment and classification of sediments according to their risk potential, and proposals for an economically and ecologically acceptable handling of sediments of different classes. Peripheral conditions had to be taken into account. These are national regulations as well as international recommendations and strategies for action aimed at the management of sediments and dredged material handled in the Rhine basin so far.

4 Sediment management plan for contaminated sediments

The conceptual approach is based on the recommendations of the European Sediment Network SedNet (APITZ et al. 2007) and a study of contaminant situation along the river Rhine (HEISE et al. 2004) and was developed in three steps as follows:

- Identification and classification of pollutants that are relevant in the watershed
- Identification and classification of areas with an increased pollution load
- Identification and classification of areas of risk

Relevant pollutants are the heavy metals Cd, Cu, Hg, Ni, Pb, Zn and organic compounds like Benzo(a)pyrene (for PAH), HCB, PCB 153 and PCB (Sum of 7). The assessment of the sediment pollution was carried out on basis of the ICPR target values and a five step classification was chosen (concentration steps as a multiple of the ICPR target values - see table 2)

Table 2
Five step classification taken ICPR target values (class 1) as basis

Pollutant	Unit	Class 1	Class 2	Class 3	Class 4	Class 5
Cd	mg/kg	≤ 1	> 1 - 2	> 2 - 4	> 4 - 8	> 8
Cu	mg/kg	≤ 50	> 50 -100	> 100 - 200	> 200 - 400	> 400
Hg	mg/kg	≤ 0,5	> 0,5 - 1	> 1 - 2	> 2 - 4	> 4
Ni	mg/kg	≤ 50	> 50 -100	> 100 - 200	> 200 - 400	> 400
Pb	mg/kg	≤ 100	> 100 - 200	> 200 - 400	> 400 - 800	> 800
Zn	mg/kg	≤ 200	> 200 - 400	> 400 - 800	> 800 - 1600	> 1600
Benzo(a) pyren	mg/kg	≤ 0,4	> 0,4 - 0,8	> 0,8 - 1,6	> 1,6 - 3,2	> 3,2
HCB	µg/kg	≤ 40	> 40 - 80	> 80 - 160	>160 - 320	> 320
PCB 153	µg/kg	≤ 4	> 4 - 8	> 8 - 16	>16 - 32	> 32
PCB (Sum of 7)	µg/kg	≤ 28	> 28 - 56	> 56 - 112	> 112 - 224	> 224

After detailed data analysis of the sediment and suspended sediment contamination along the Rhine and discussion by the expert group the value for relevant sediment pollution was set with excess of the 4-fold value of the Class 1. This value is substantial higher than values which can be found nowadays in suspended sediments along the river Rhine but in this way it is intended that measures lead to a significant improvement of contaminant situation. In the second step the appropriate amount of polluted sediment was set to >1000 m³. In the third step the risk of remobilization of polluted sediments is assessed by adequate flood event investigations or by comparison of critical shear stress of the sediments with shear stress at high flood HQ_{10} The whole rule-based evaluation for the identification of areas of risk is shown in figure 1.

As seen in figure 1 three types of remobilization risk are distinguished and in the range from 3A to 3C there is an increasing control of the risk of remobilization. For assessing the risk of remobilization also national or international legal framework (step 4 in figure 1) is taken into account.

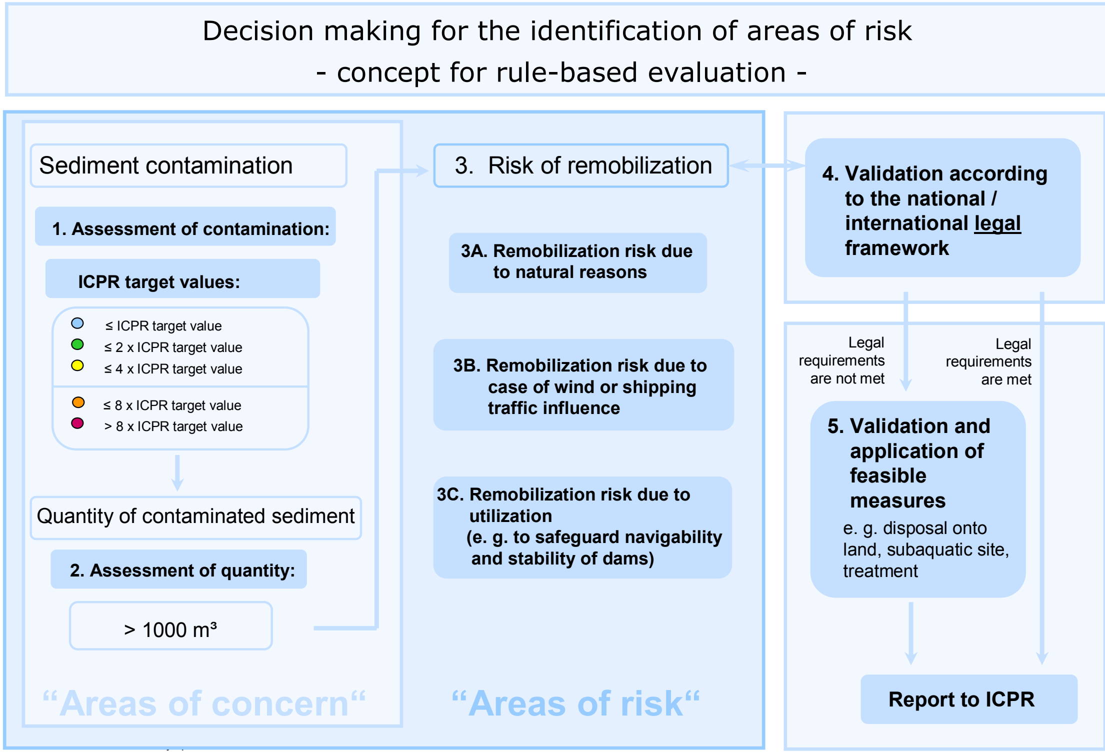

Figure 1: Scheme of a rule-based evaluation of areas of risk

Step 4 an 5 are site-specific and are addressed in reference sheets for each area of risk and each area of concern. The reference sheets had been designed with the following information:

- Summary of Data
- Risk assessment
- National legislative framework
- Recommendations of measures in the Rhine basin management plans.

In a further chapter of the reference sheet the potential of remobilization and the uncertainty of data with regard to the level of pollution, the amount of polluted sediment, and the level of remobilization is discussed.

From 93 sediment sites under investigation 22 sites had been identified as areas of risk, of this 16 as type A, 2 as type B and 4 as type C. Further 18 sites had been identified as areas of concern. In figure 2 a map with the areas of risk is shown distinguishing sites with the three types of remobilisation risk.

The high contaminated sediment sites at the Marckolsheim and Rhinau barrages are recommended for remediation because these sites are a source for HCB contaminations of sediments downstream. The amount of high contaminated sediments is estimated at 300 000 to 500 000 m³ altogether. After this local remediation the level of HCB contamination in sediments of the Gambsheim and Iffezheim barrages will decrease within a few years.

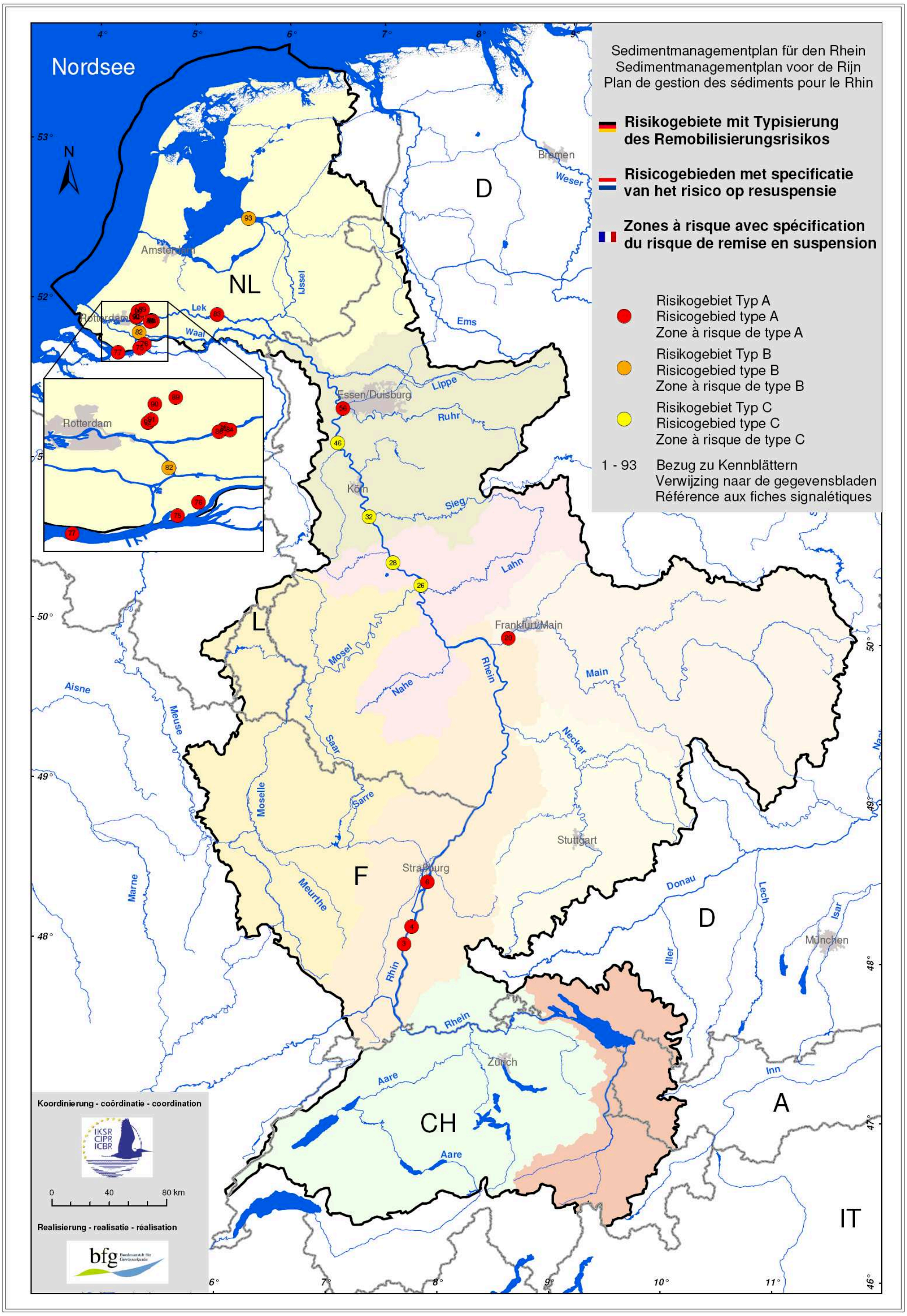

Figure 2: Map of areas of risk (numbers correspond to numbers of reference sheets)

Summary

An ICPR expert group elaborates a comprehensive strategy for sediment management in the Rhine basin. Main objectives are a sediment management plan for contaminated sediments addressed to competent authorities in the watersheds for implementation in measure programmes according to WFD and the "improvement of sediment quality in order to relocate dredged material without harm" (Art. 3 of the ICPR Rhine Convention). The mandate of the ICPR expert group covers three points: First, to draft a management plan for contaminated sediment. This includes an inventory of relevant sediment studies so far, the determination of the extent of pollution and the quantity of polluted sediments, the assessment and classification of sediments according to their risk potential, and proposals for an economically and ecologically acceptable handling of sediments of different classes. Second, peripheral conditions to be taken into account. These are national regulations as well as inter-national recommendations and strategies for action aimed at the management of sediments and dredged material handled in the Rhine basin so far. Third, a survey of hot spots including priority action has to be provided.

The results of the ICPR research project "Investigations on resuspension risk of polluted sediments in the river Rhine and its tributaries" in the years 2000-2003 have been important for the comprehensive strategy for sediment management in the Rhine basin. The inventory of polluted sites resulted in the identification of a focal point at selected Upper Rhine barrages, which is connected with historical sediment contamination of hexachlorobenzene (HCB). Further investigations prove, that especially in the head-waters of the Marckolsheim and Rhinau barrages sediment contamination is a source for ongoing pollution downstream.

The conceptual approach for the sediment management plan is based mainly on the recommendations of the European Sediment Network SedNet. The concept for a rule-based evaluation was developed in three steps:

- Identification and classification of pollutants that are relevant in the watershed
- Identification and classification of areas with an increased pollution load
- Identification and classification of areas of risk

Relevant pollutants are six heavy metals and organic compounds like PAH, HCB and PCB. A five step classification of the sediment pollution was carried out on basis of the ICPR target values. The risk of remobilization of polluted sediments is assessed by adequate flood event investigations or by comparison of critical shear stress of the sediments with shear stress at high flood. From 93 sediment sites under investigation 22 sites had been identified as areas of risk, further 18 sites had been identified as areas of concern. The high contaminated sediment sites at the Marckolsheim and Rhinau barrages are recommended for remediation because these sites are a source for HCB contaminations of sediments downstream.

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